Fabrication and Imaging of 2D Nanomembranes and Graphene using

Outline:

Part I : Fabrication of 2D carbon nanostructures

Nanomembranes from SAMs

-Graphene and Graphenoids

-Nanoribbons and Nanosieves

Chemical Lithography

-Polymer Carpets

-Protein Biochips

-Janus Membranes

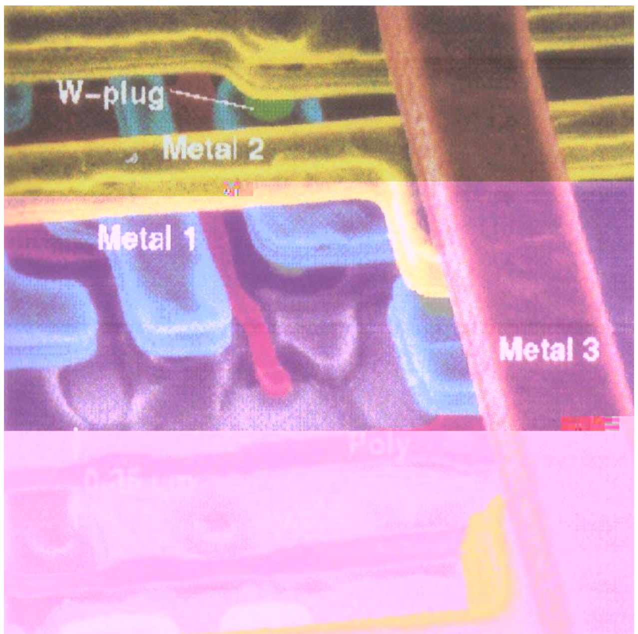
Part II : Helium Ion Microscopy

Basics

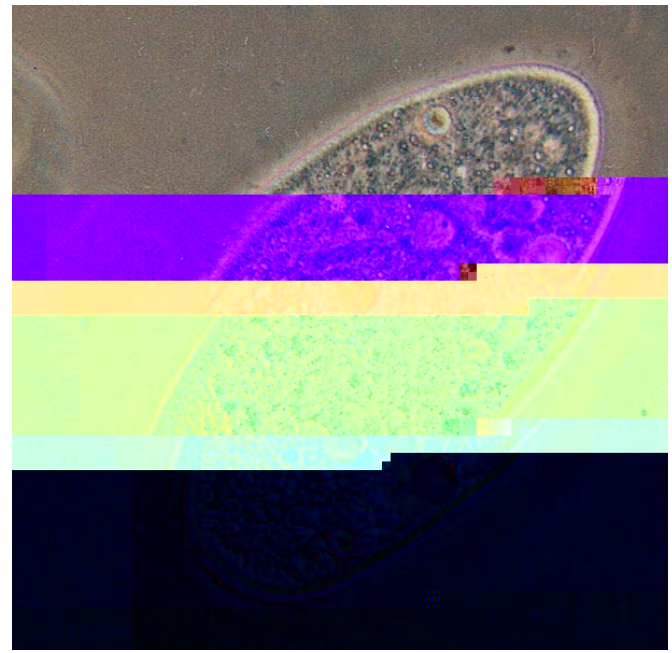
Nanomembranes and BioImaging

Concepts of Nanostructure Fabrication

Integrated circuit
Lithography
(physics, engineering)

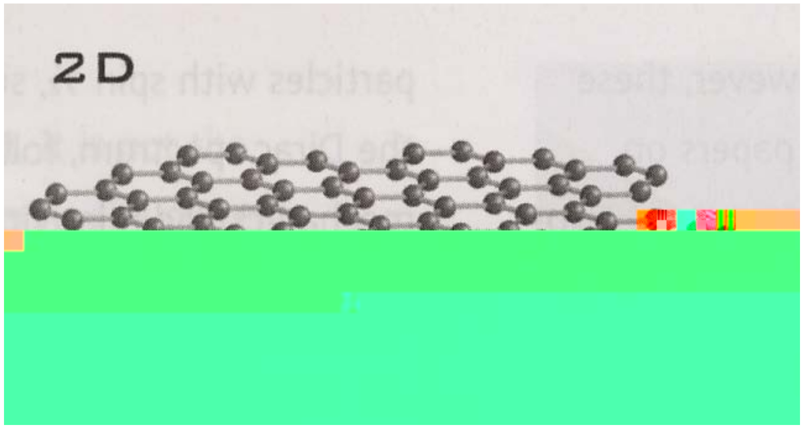


Eukaryotic cell
Self-assembly
(chemistry, biology)



Objective: Building (bio)functional molecular nanostructures with lithography and self-assembly

2-Dimensional Carbon Nanostructures



<u>Graphene:</u>

solid state, hard

<u>Fabrication procedures :</u>

•*Exfoliation of graphite/HOPG*

•*Epitaxy of SiC/TiC*

•*Oxidation/reduction of graphite*

•*CVD of hydrocarbons*

<u>Hard to functionalize</u>

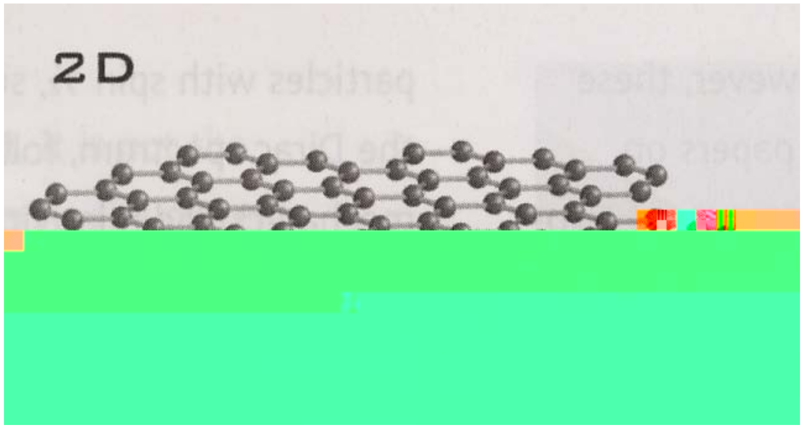
<u>Cell membranes:</u>

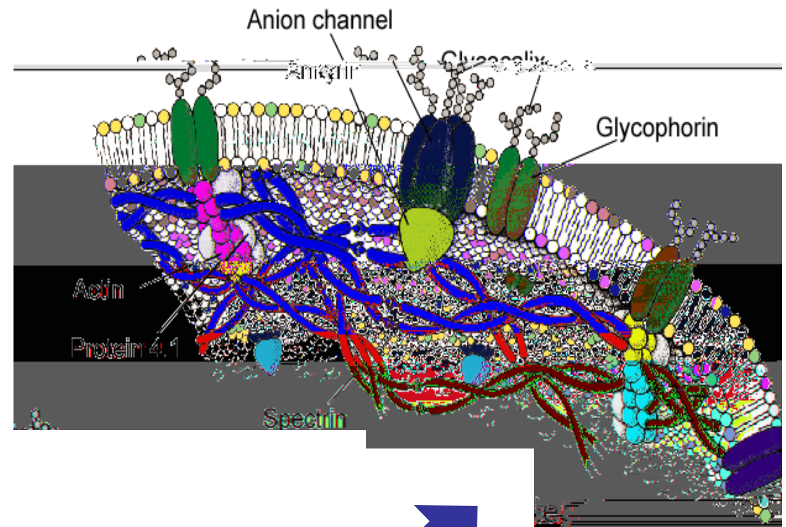
molecular, soft, directional

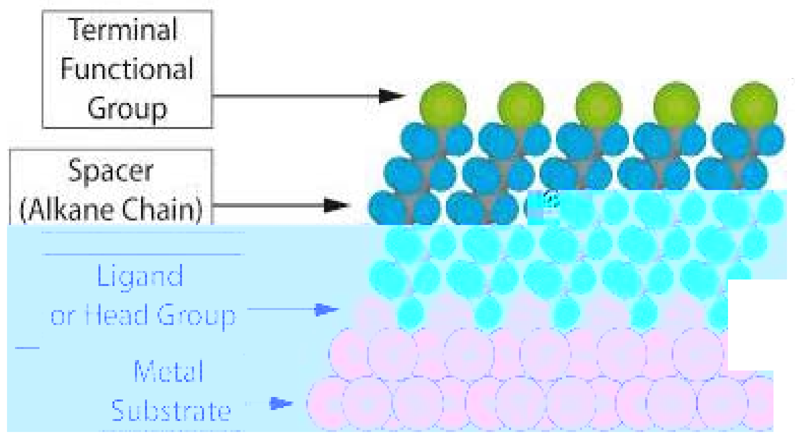
<u>Fabrication procedures :</u>

•*Self-Assembl4 Tc T(•MC /Texb6T.*

2-Dimensional Carbon Nanostructures







<u>Self-Assembled Monolayer (SAM):</u>

molecular, soft, directional

<u>Fabrication:</u>

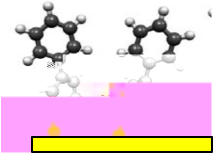
Surface chemistry, Intermolecular interactions, lateral ordering, 2D-crystallization

A molecular path to two-dimensional carbon nanostructures

Molecules | **Solid substrates**

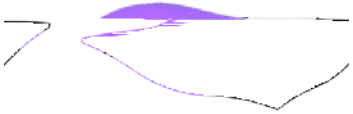
self-assembly

Self-Assembled Monolayers (SAMs)



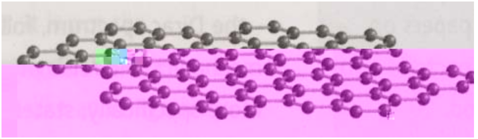
cross-linking by electron-beam

Carbon Nanomembranes



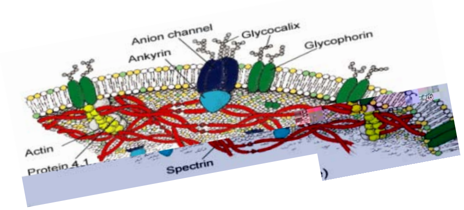
pyrolysis

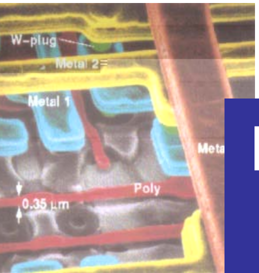
Graphene and Graphenoids



chemical, biological functionalization

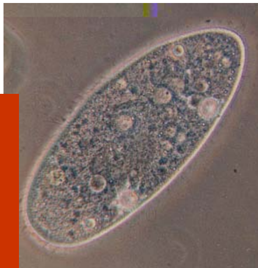
Functional Membranes





Electronics, NEMS, Sensors, …

Biomimetic, Medical, Biosensors,…

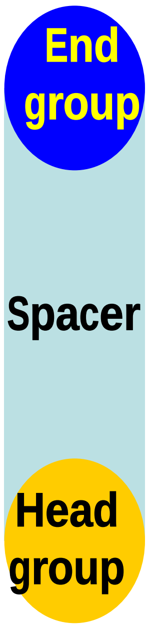


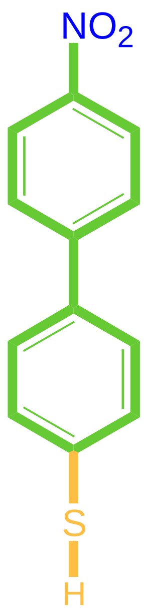
Self-Assembled Monolayers (SAMs)

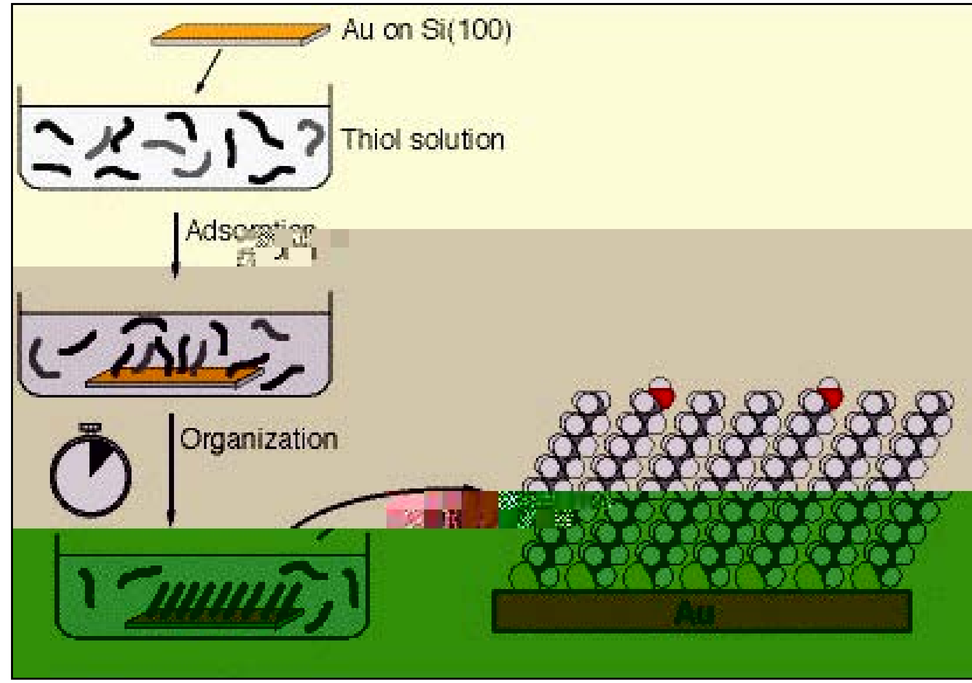
-H
-OH
-NO_2
-NH_2
...

Alkyl
Phenyl
...

-SH
-$SiCl_3$
...







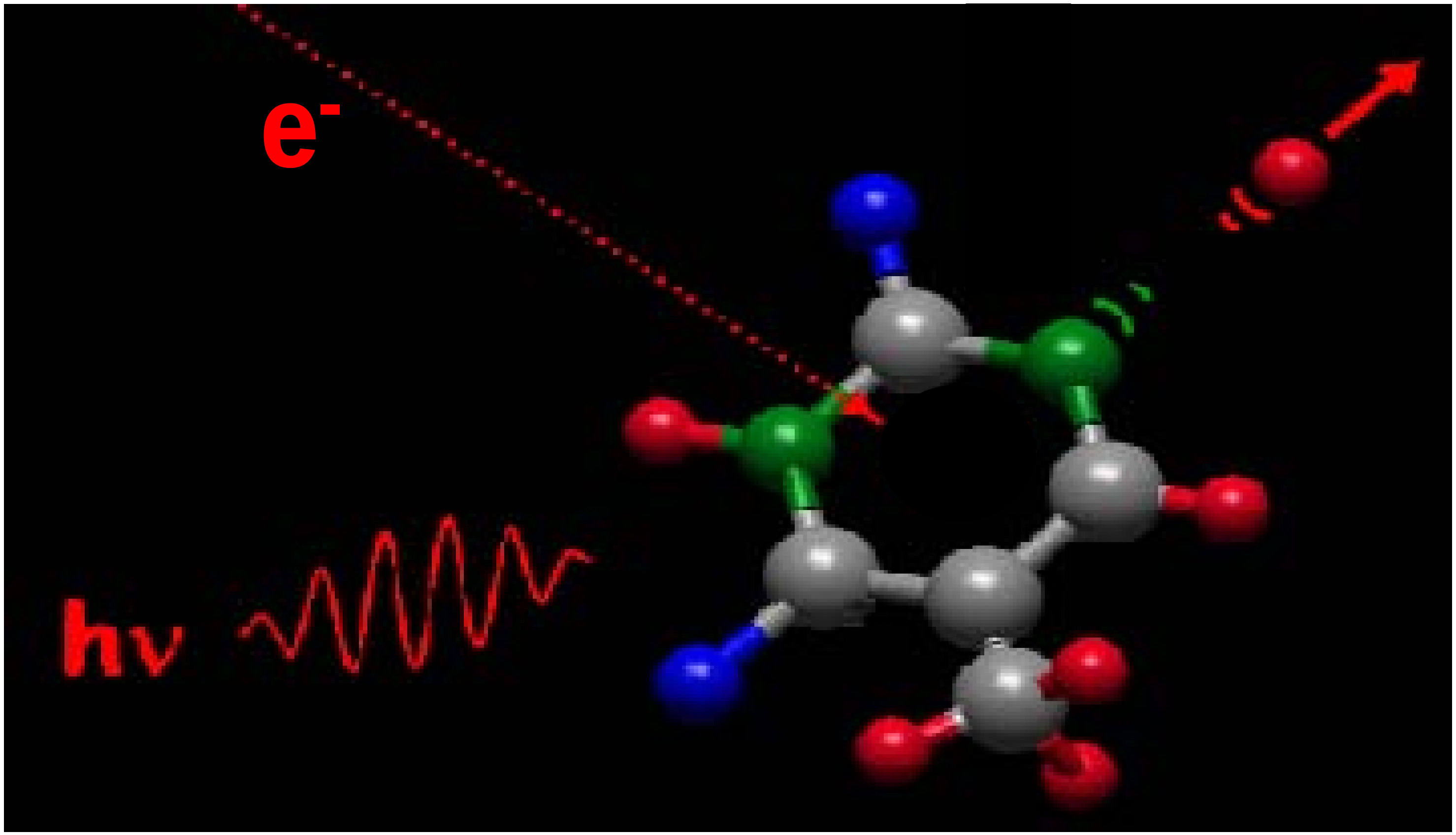
soft film on hard substrate

Fabrication procedures and conditions:

- *Liquid state, solutions*
- *ambient temperature and atmospheric pressure*
- *crystallization, equilibrium*

Easy to functionalize by choice of molecules and substrate

Electron and Photon induced Chemical Control

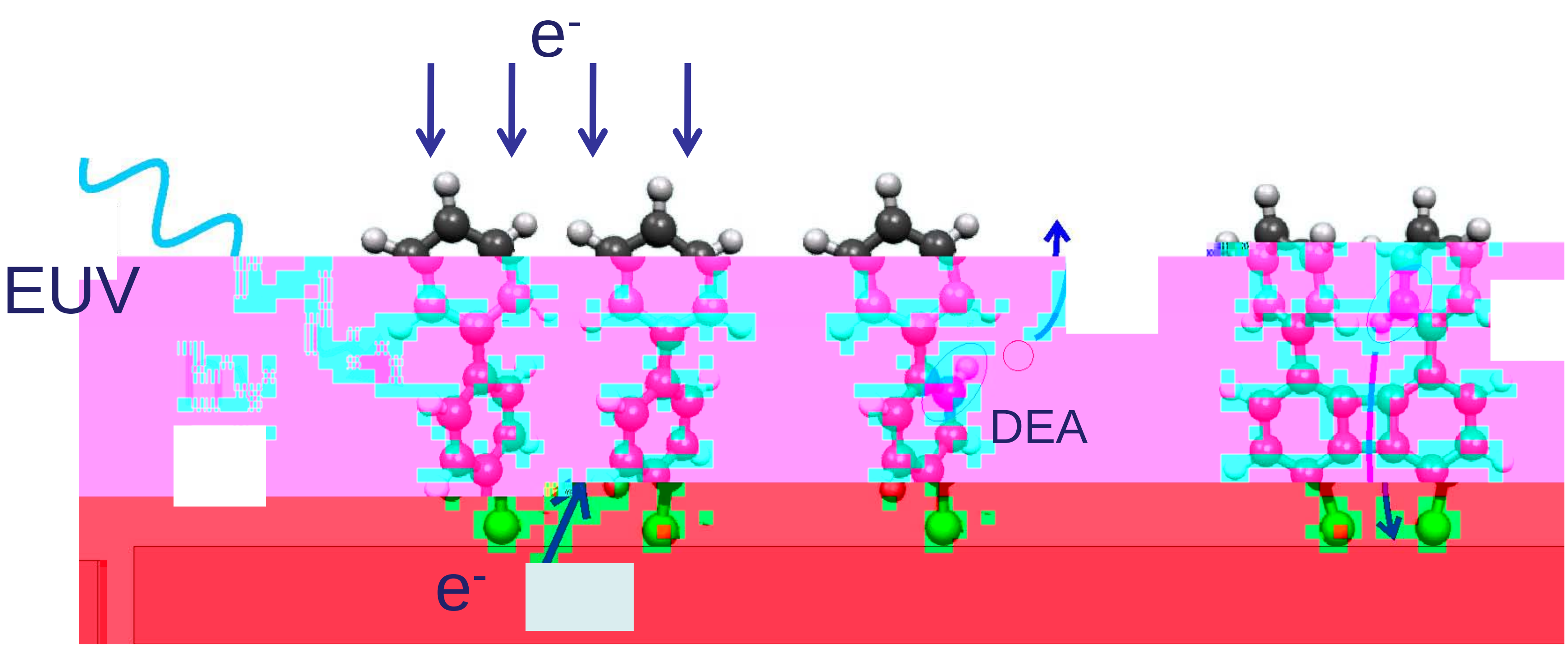


Electron-molecule interaction:

... Dissociative Electron Attachment (DEA) via Transient Negative Ion (TNI)

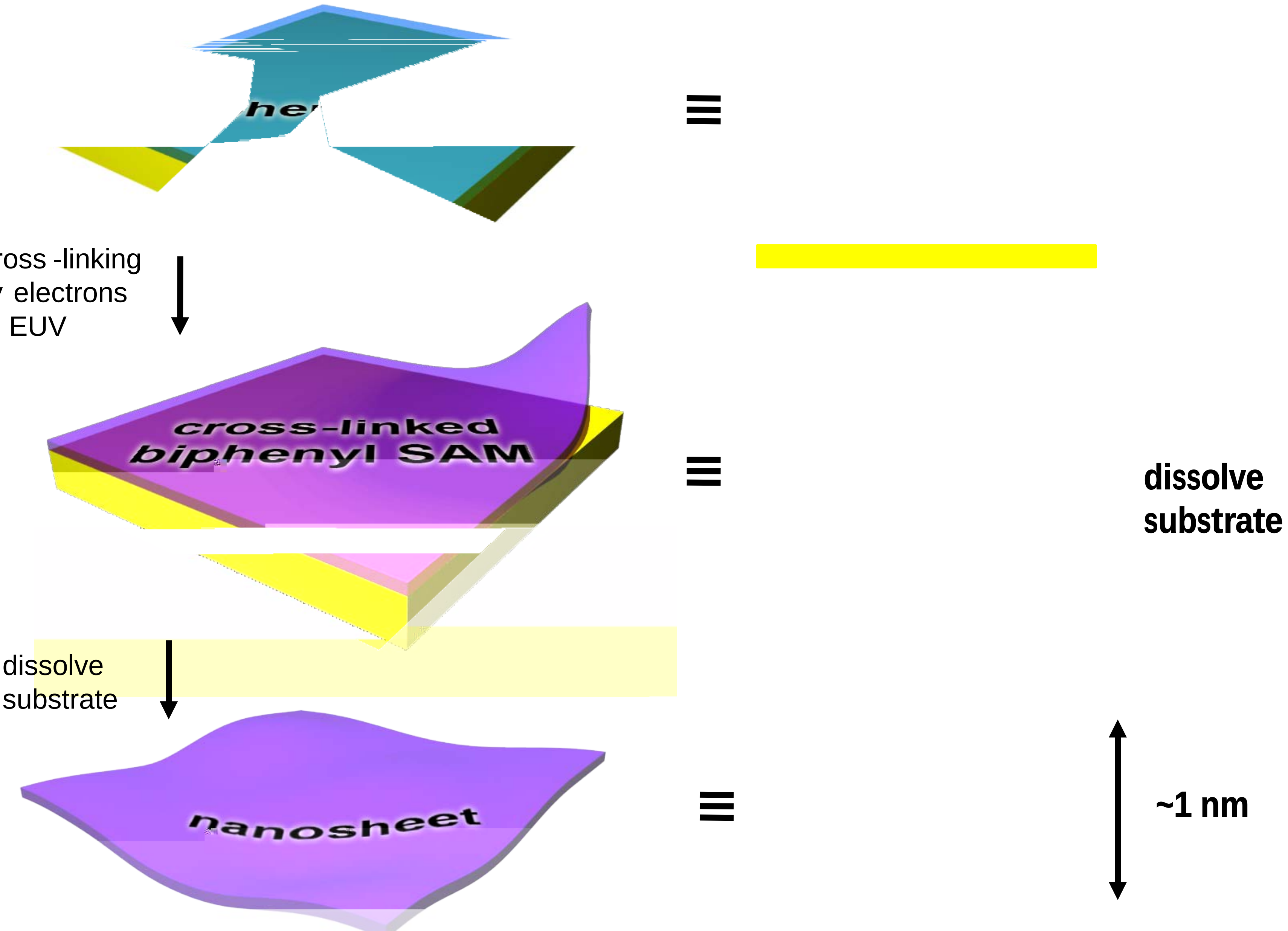
... requires low electron energies... typically below 10 eV

Electron and Photon induced Chemical Control in SAMs



W. Geyer et al. Appl. Phys. Lett 75, 2401 (1999)
W. Eck et al. Adv. Mater. 12, 805 (2000)
A. Turchanin et al. Small 3, 2114 (2007)
A. Turchanin et al. Langmuir 25, 7372 (2009)

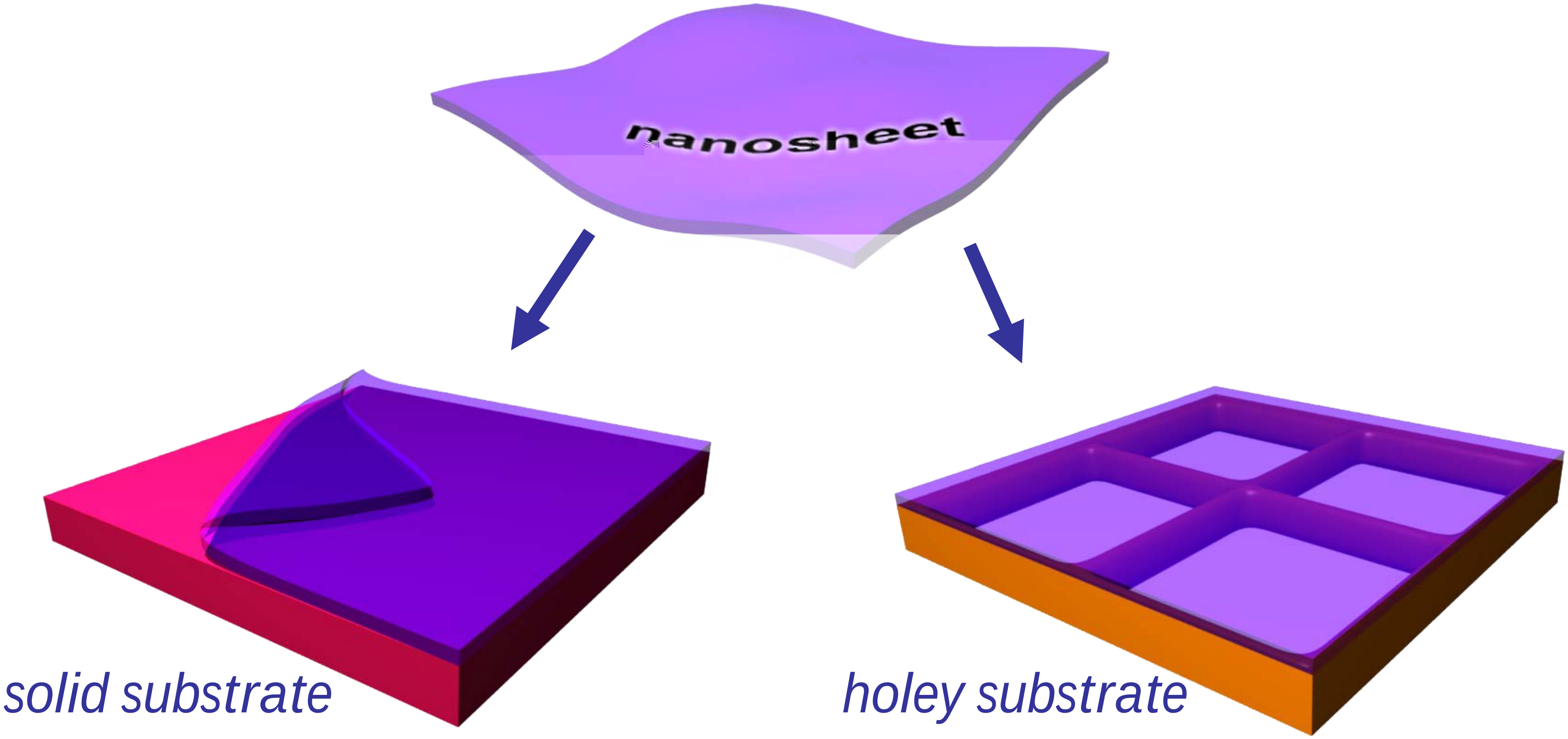
Preparation of Nanomembrane



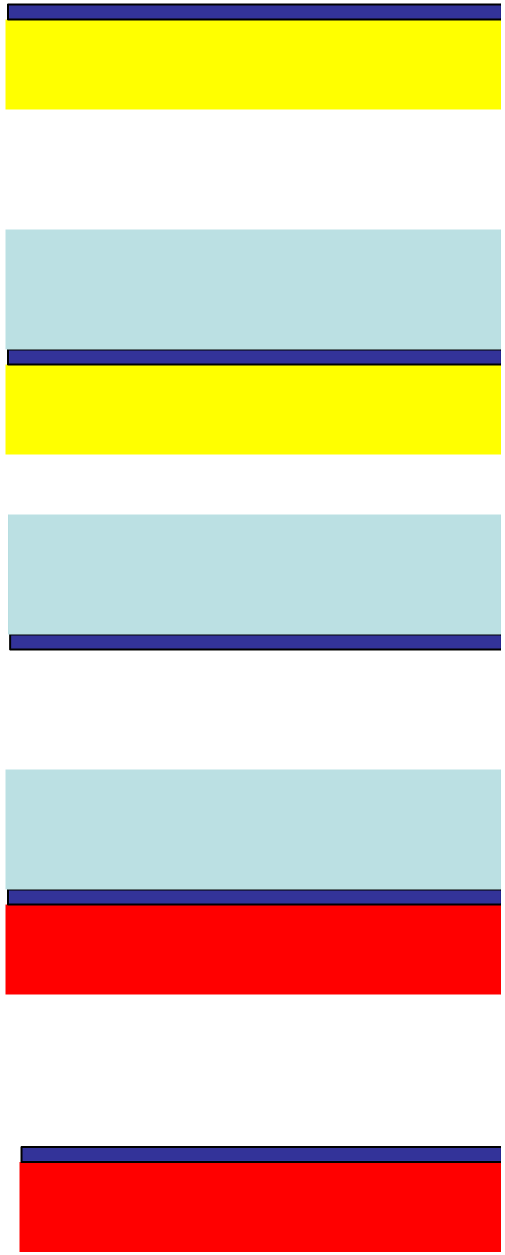
Cross -linking
by electrons
or EUV

dissolve
substrate

Preparation of Nanomembrane



Transfer of carbon nanomembrane, process



CNM / Substrate 1 (Au, SiN, ...)

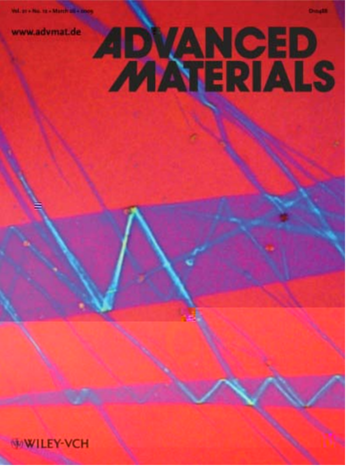
Coat with transfer medium

Dissolve substrate 1

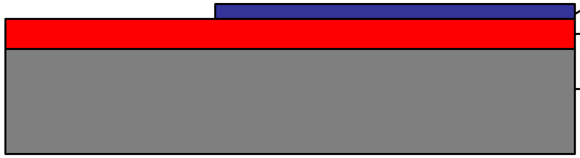
Place on substrate 2

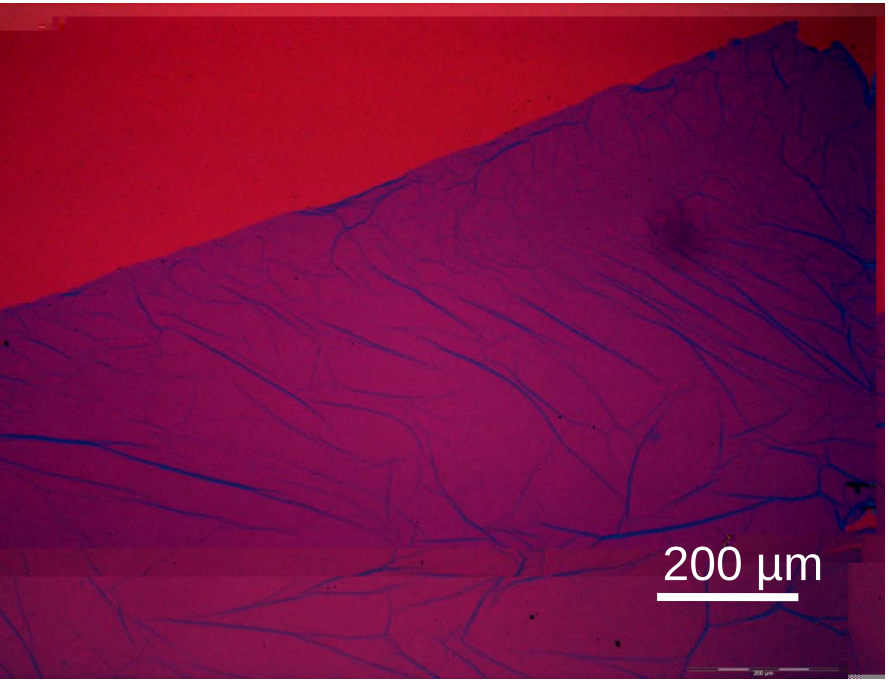
Dissolve transfer medium

CNM / Substrate 2 (SiO, Si, ...)



1 nm thick Membrane on SiO/Si: Interference Contrast



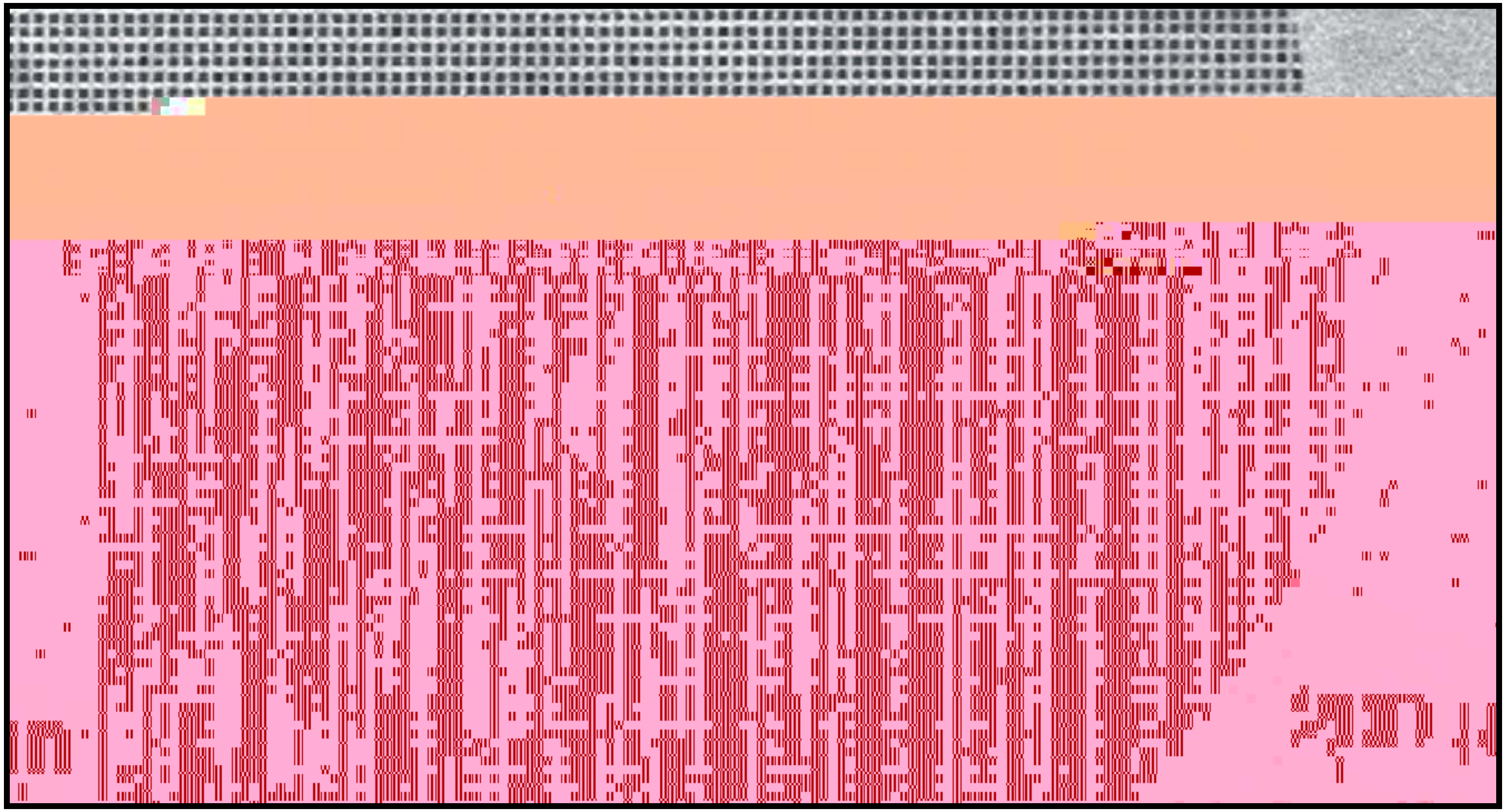


optical micrograph

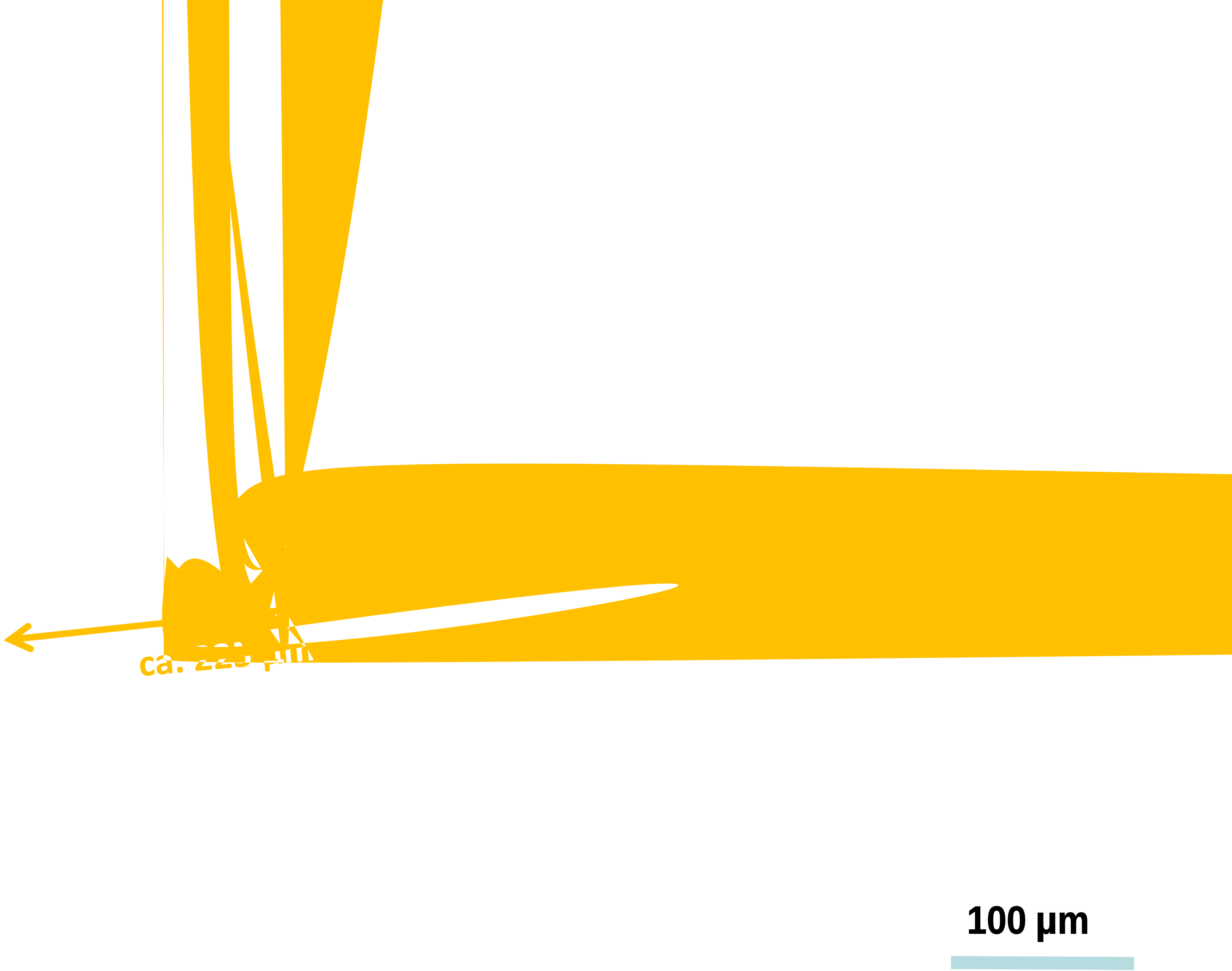
photograph

Nanosheet on TEM grid

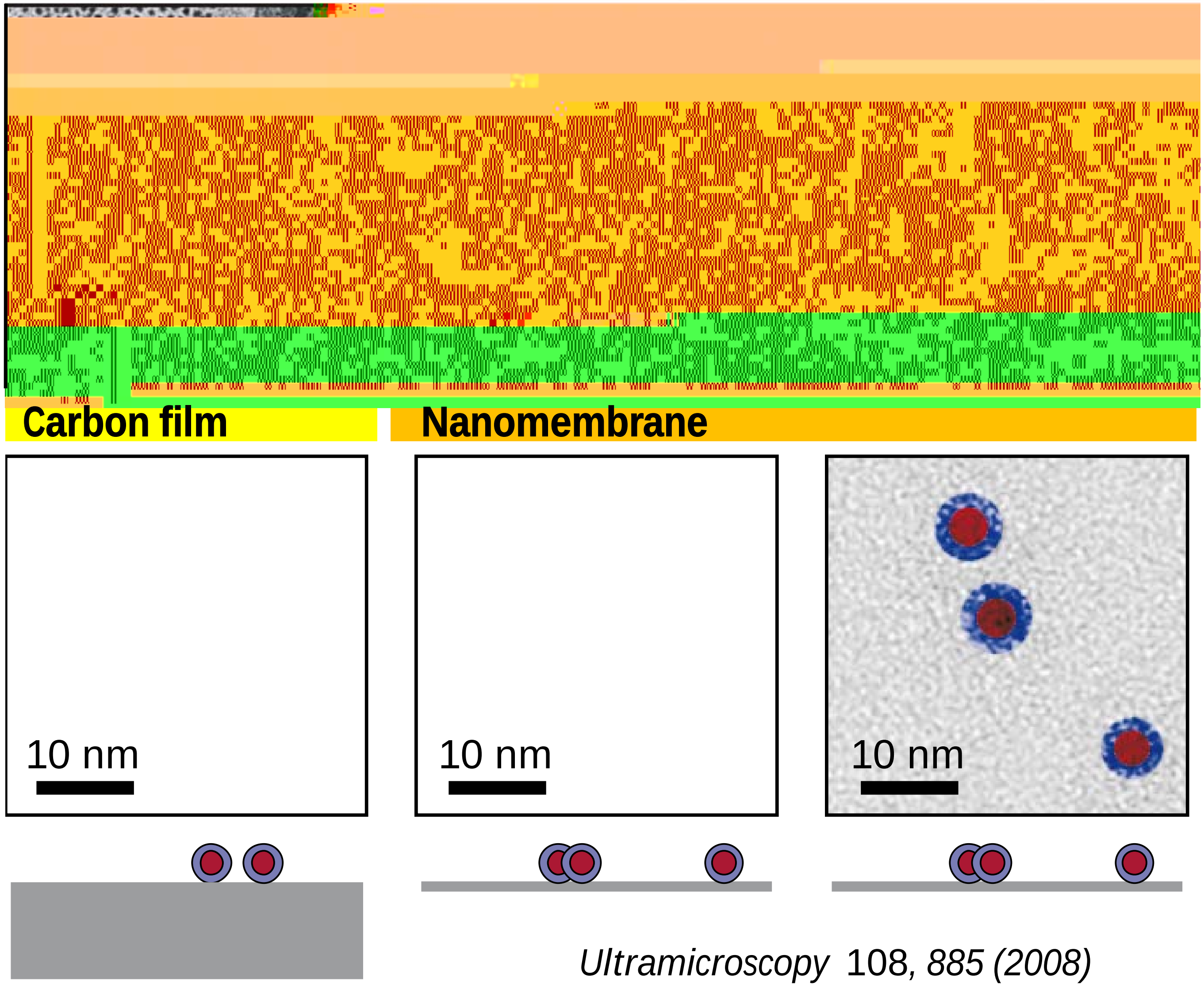
TEM grid (Au 1500mesh), SEM Image



Nottbohm et al., Ultramicroscopy 108, *885 (2008)*


100 µm

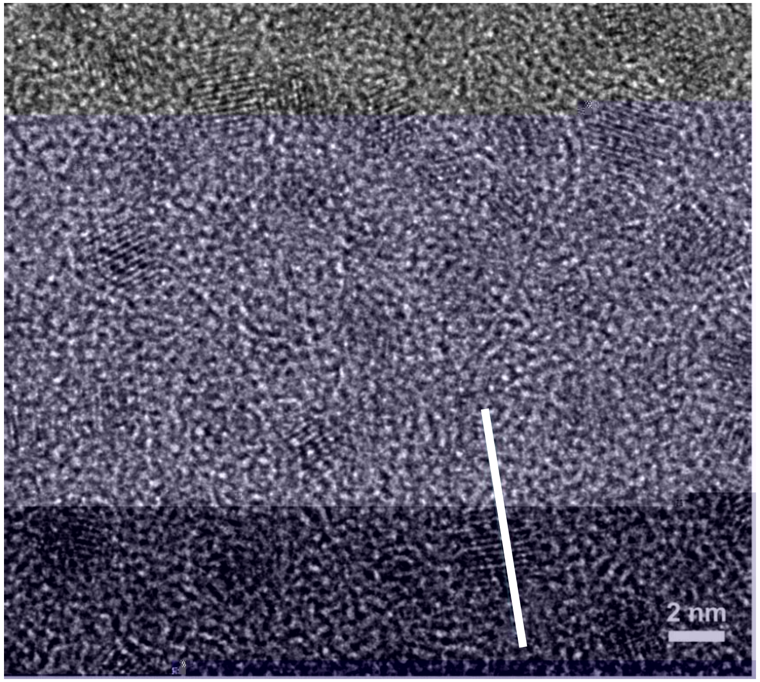
Nanomembrane supports for HRTEM: Imaging of - Co nanoparticles (ca. 4 nm)



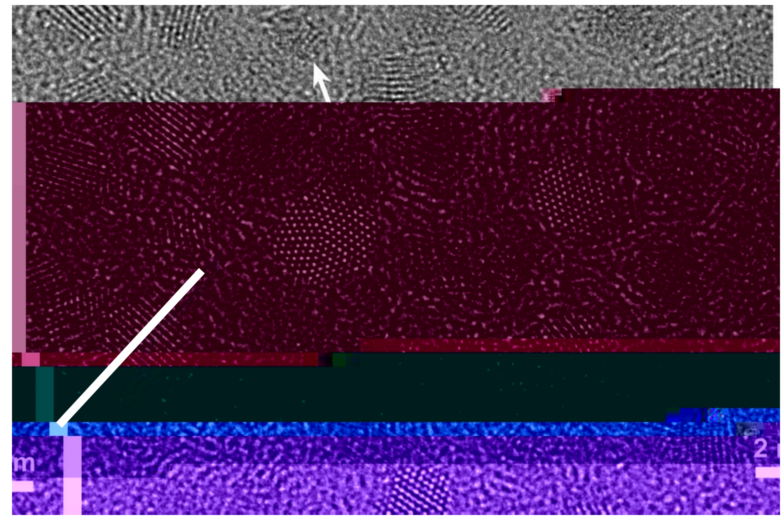
Ultramicroscopy 108, *885 (2008)*

TEM - Au_{55} Cluster

Carbon film



Nanosheet



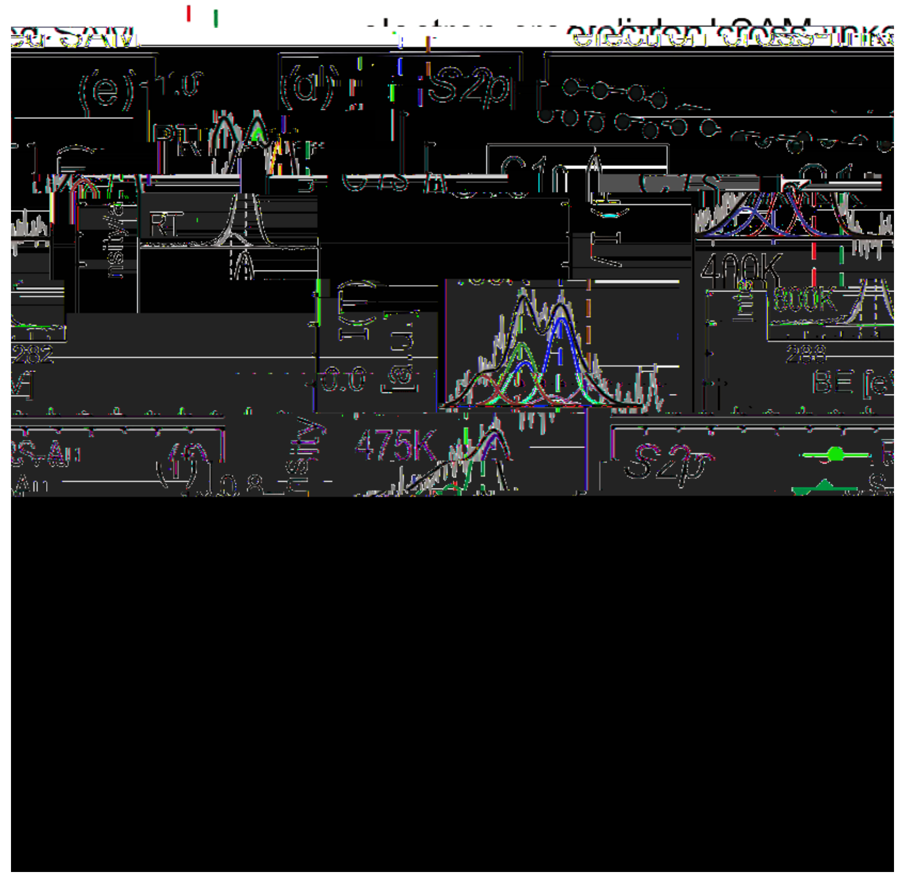
(J. Mayer, A. Sologubenko, RWTH Aachen)

Thermal Properties of Carbon Nanomembranes

Heating of biphenylthiol nanosheet on SiO_2-Si in UHV

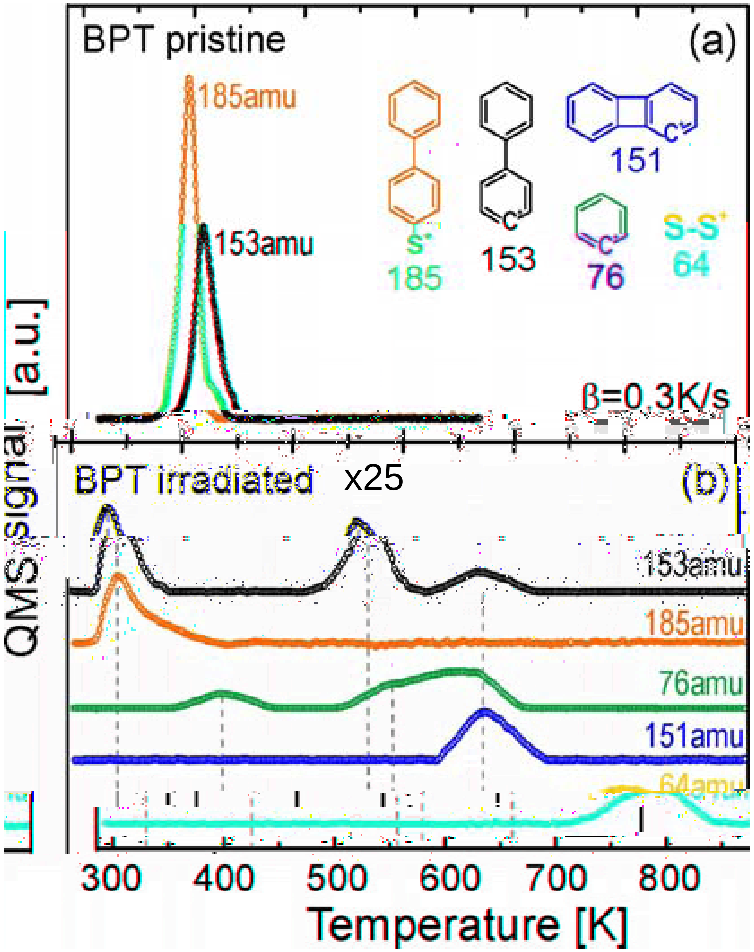
Appl. Phys. Lett. **90,** 053102 (2007)

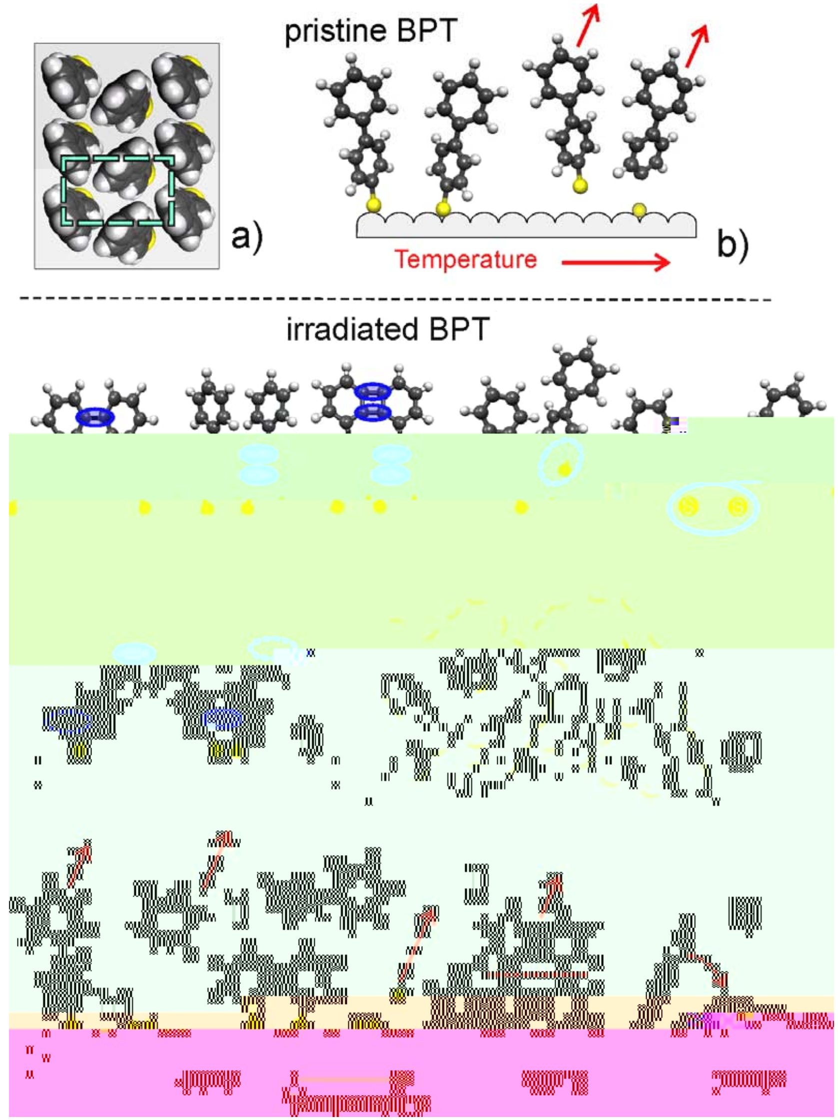
Heating of pristine and cross-linked BPT SAMs (XPS)



A. Turchanin et al. Langmuir 25, 7372 (2009)

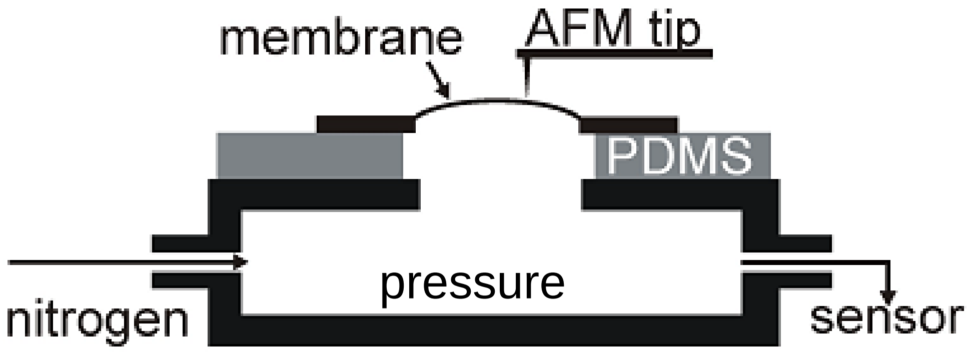
Heat induced molecular desorption

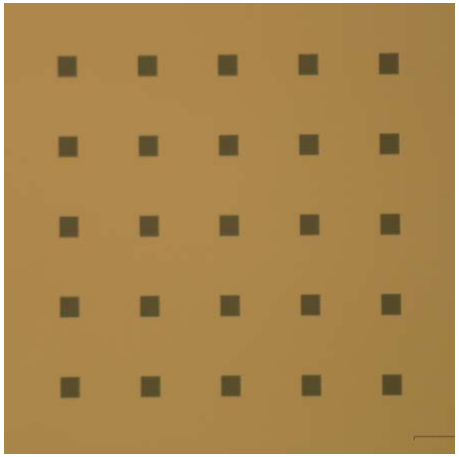




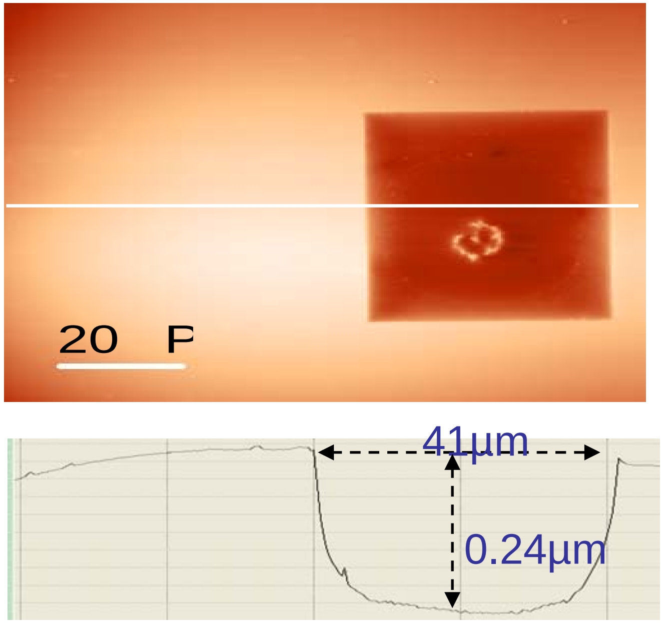
A. Turchanin et al. Langmuir 25, 7372 (2009)

Membrane mechanics: Bulge Tests

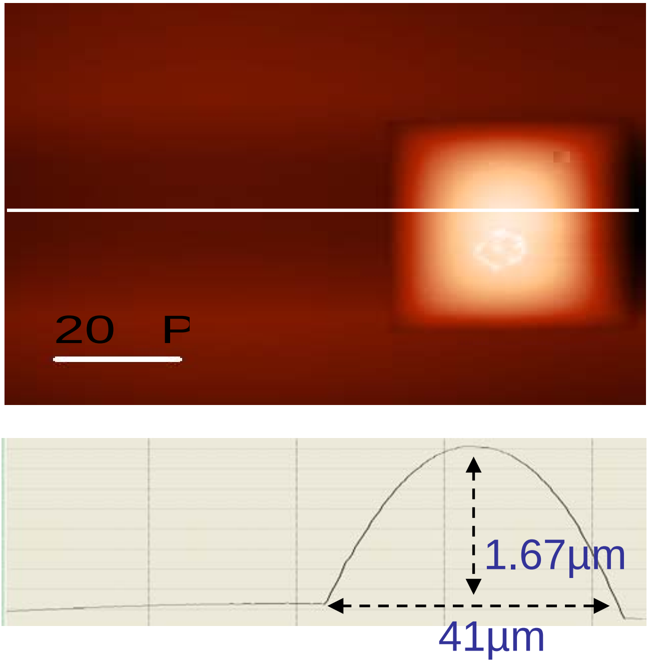




p=0



p=750Pa



Mechanical properties of nanomembranes

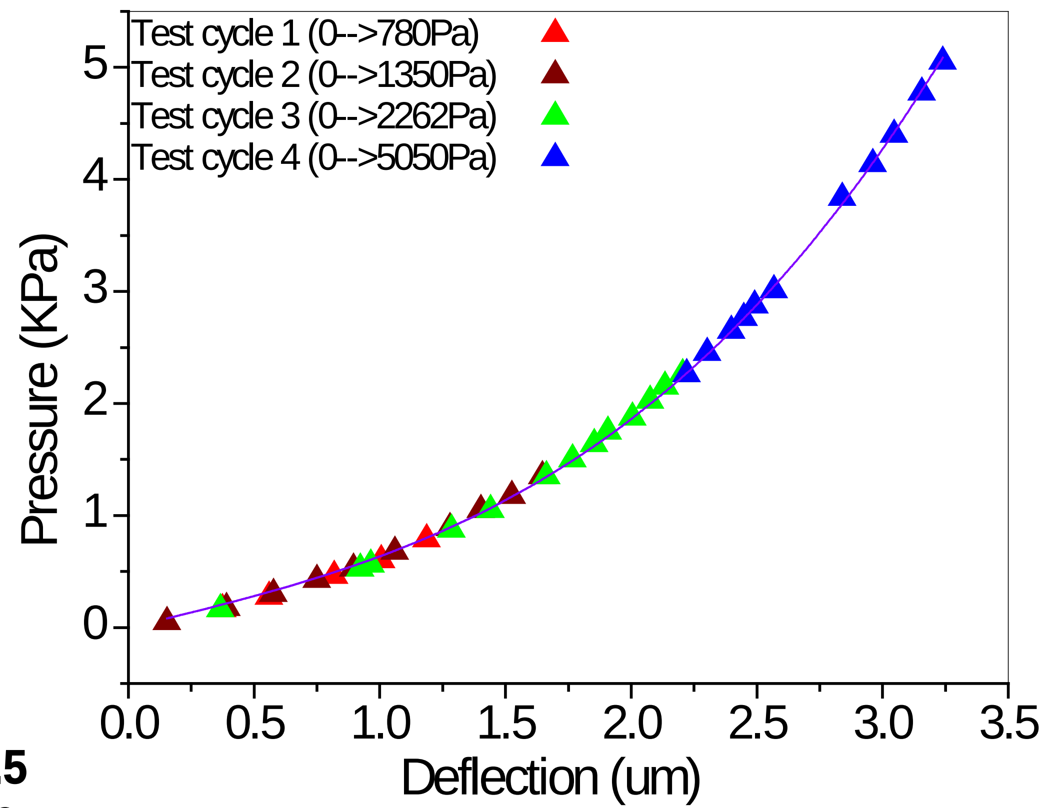
Pressure-deflection relationship for a stressed nanomembrane:

$$P \quad P_1 \quad P_2 \quad \frac{Et}{a^4(1 \quad Q)} h^3 \quad \frac{V_0 t}{a^2} h$$

J.J.Vlassak and W.D. Nix, J. Mater. Res. 7 (1992) 3242

t=1.5nm: thickness
v=0.35: Poisson's ratio
E=Young's modulus
V_0 = residual stress
a: half-width
b/a: aspect ratio

E = 10.0 GPa
V_0= 40.0 MPa



some E values (Gpa):
rubber 0.01....0.1, polystyrene 3.0.....3.5
copper 110... 130, diamond 1050...1200

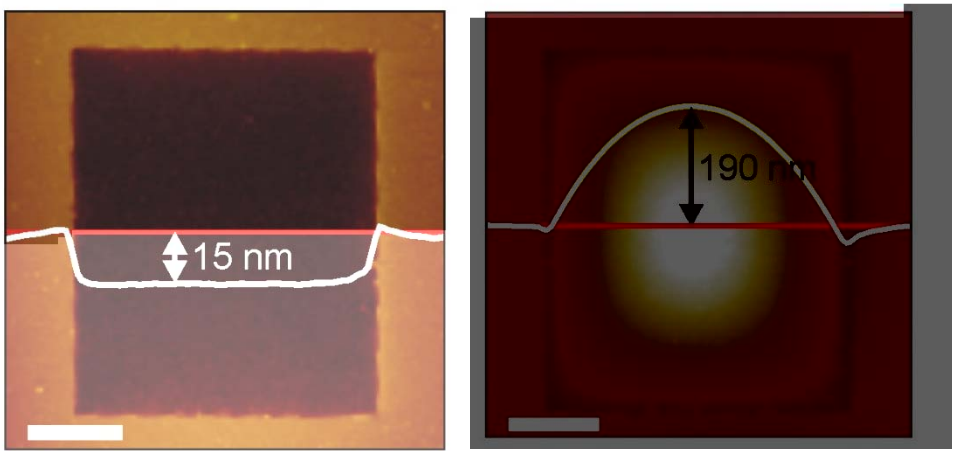
Comparison with other Free-standing Nanomembranes

Freestanding nanomembranes	Thickness (nm)	Fabrication Method	Young's Modulus (GPa)	Tensile Strength (MPa)
Nanocomposite membranes [1]	**55**	Spin-assisted layer by layer assembly	**8± 3.5**	**40…100**
IPNs hybrid nanomembranes[2]	**35**	Spin-coating and polymerization	**N.A.**	**105**
Nanomembranes (epoxy resin)[3]	**20**	Spin-coating and baking	**N.A.**	**30**
Nanomembranes[4] (melamine,phthalic, rethane,epoxy)	**19…24**	Spin-coating, irradiation, baking	**1.2…3.5**	**10…22**
Carbon Nanomembrane	**1.5**	**Self-assembly & cross-linking**	**10**	**150…420**

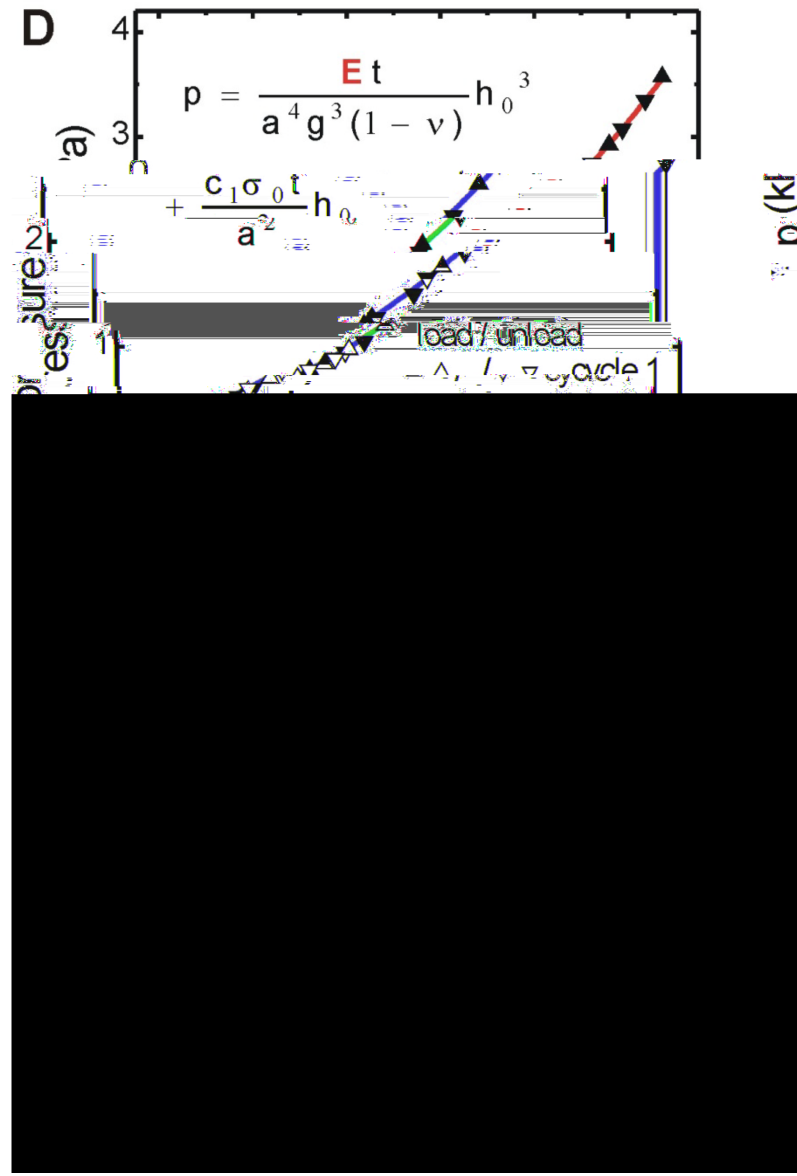
[1] Nature Materials 3 (2004) 721; Advanced Materials 17 (2005) 1669
[2] Nature Materials 5 (2006) 494

Effect of Annealing on Young's Modulus

P=0 Pa P=450 Pa



(annealed at ~900 K)



- Young's modulus increase from ~10 GPa to ~45 GPa after heating at ~1000K

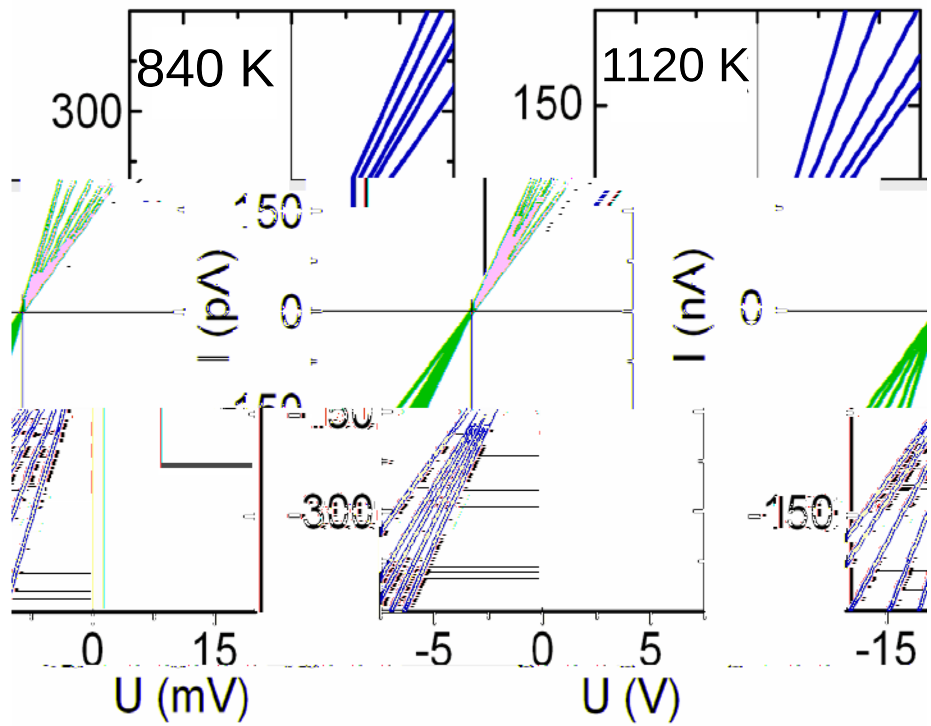
- Residual strain reduced from ~0.9 % to ~0.35 %

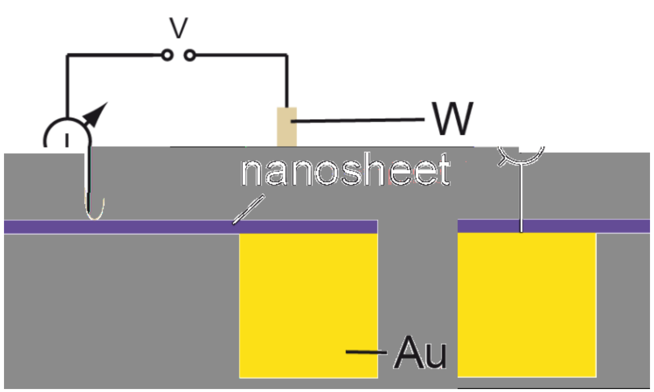
- Structural transformation

Adv. Mater. **21,** 1233 (2009)

Electrical Characterization of Nanomenbranes:

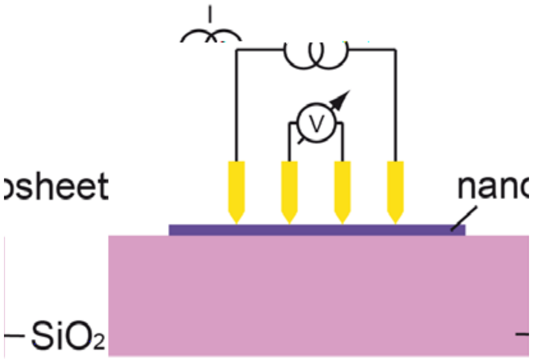
Electrical Characterization of Nanomenbranes: 2-point measurement of free-standing membrane in UHV SEM/STM



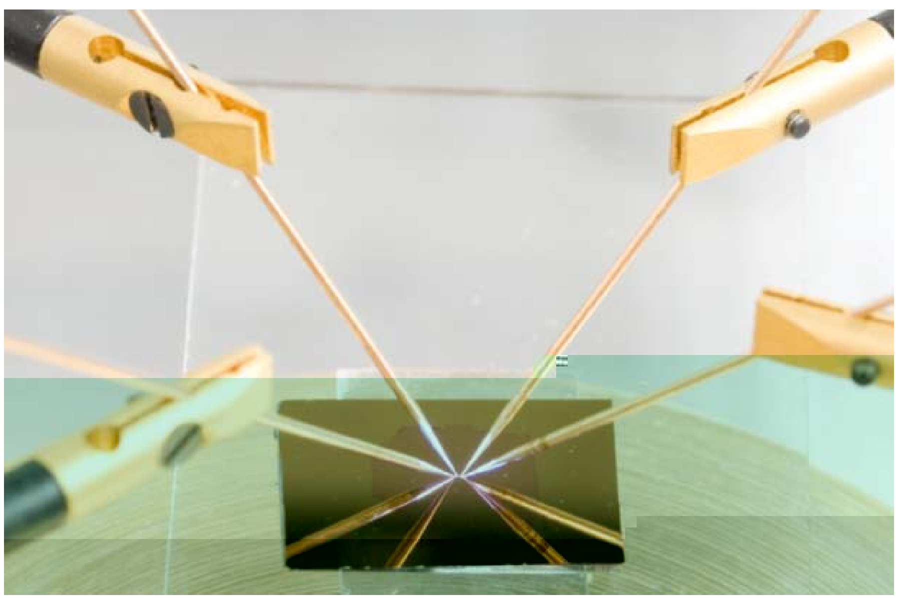


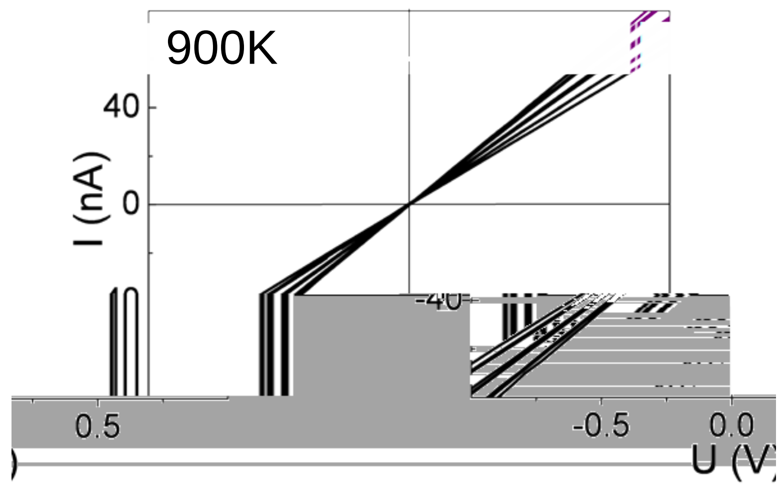
Turchanin et al. Adv. Mater. **21,** 1233 (2009)

Electrical Characterization of Nanomenbranes: 4-point measurement of supported membrane on SiO-surface

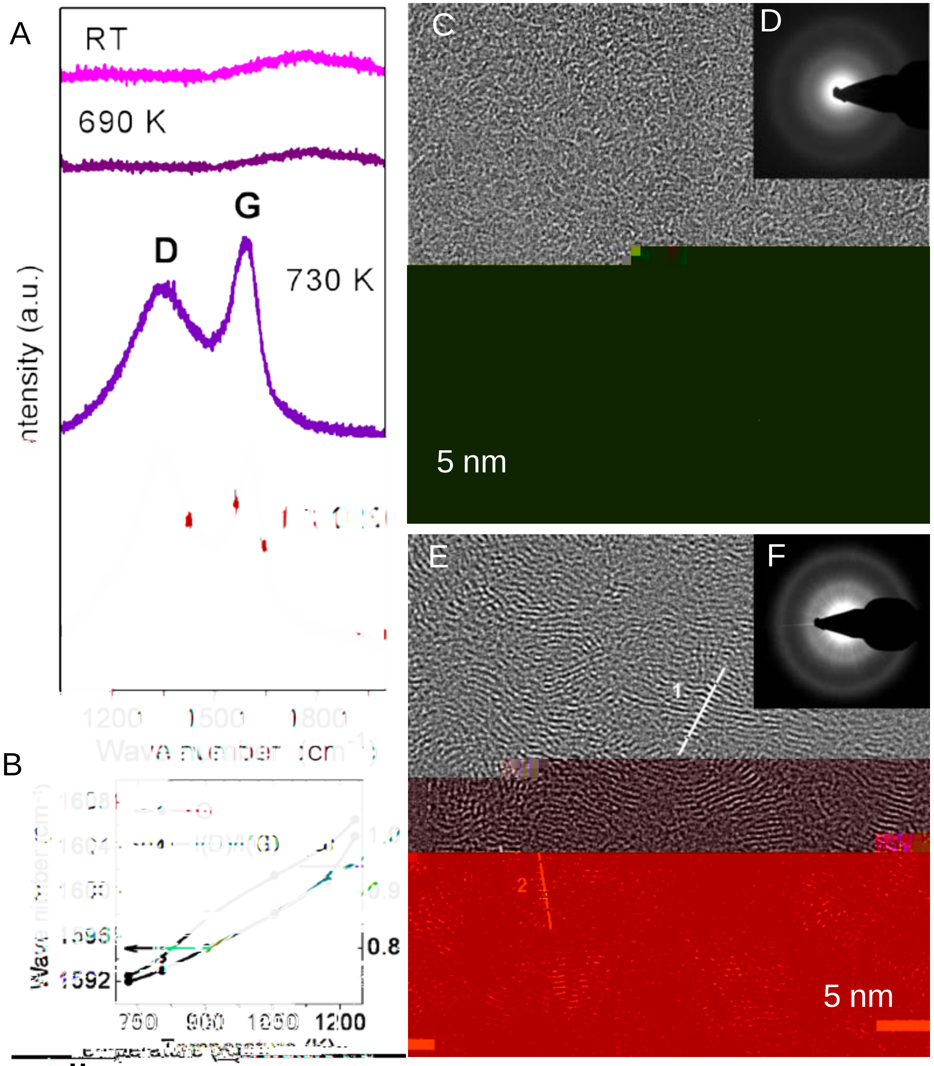


$$\rho_S = \frac{\pi}{\ln(2)}\frac{V}{I} = 4.532\frac{V}{I}\ \Omega/\text{square}$$





Structural transition (insulator to conductor) in nanomembrane (Raman spectroscopy and TEM):

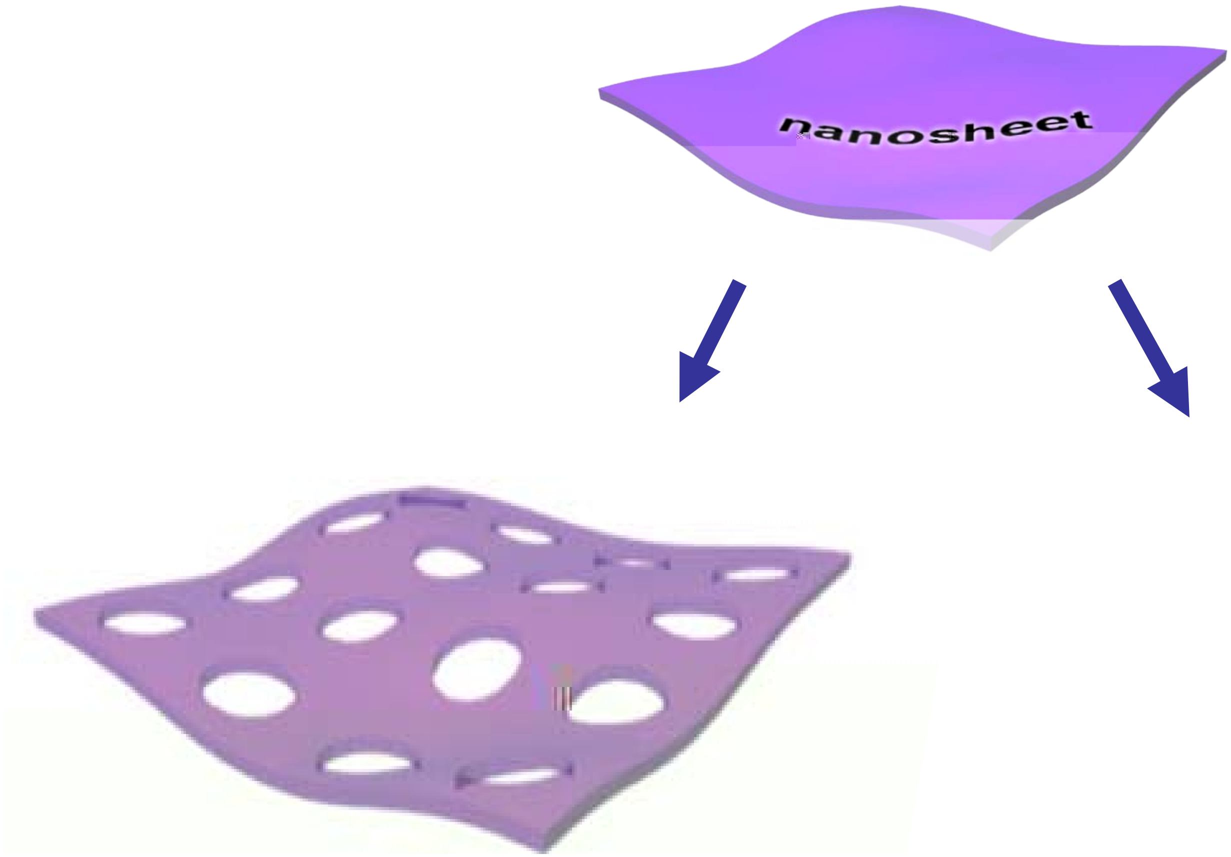


ŸFormation of nanocrystalline graphene

ŸTunable electrical properties !!

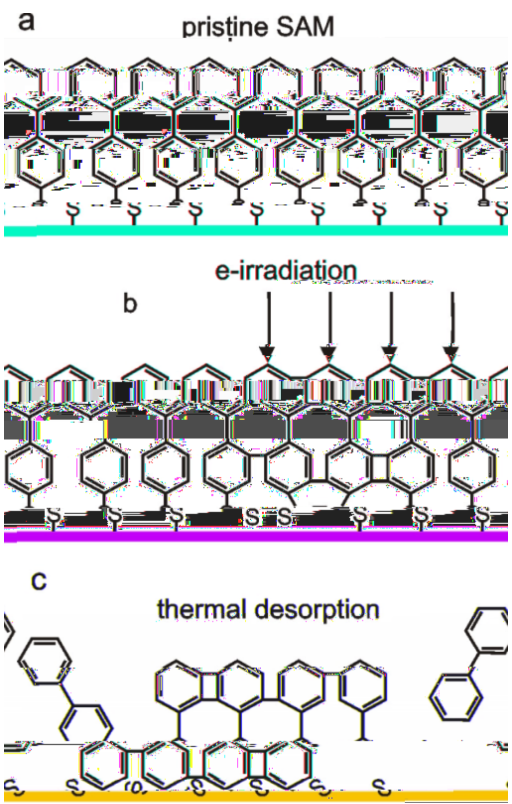
Adv. Mater. **21,** 1233 (2009)

Perforating and functionalizing carbon nanomembranes



Thermal Desorption Lithography (TDL): Fabrication of Graphenoid Nanoribbons

25 Irradiation dose (mC/cm ^{2}) 100



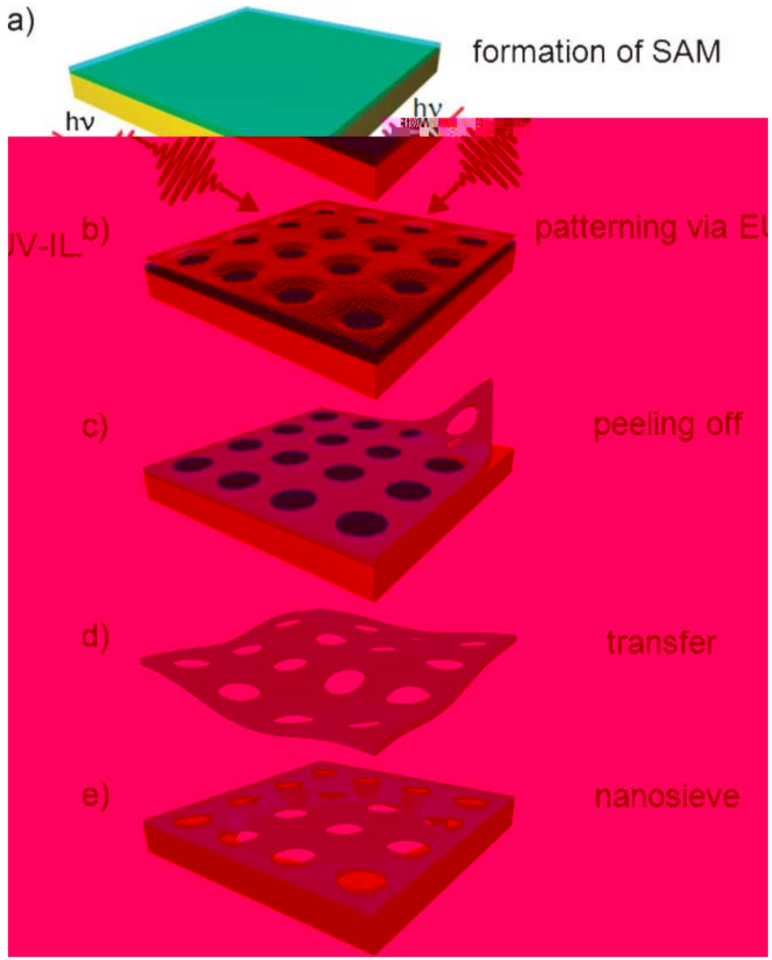
250 Lateral dimension (nm) 10

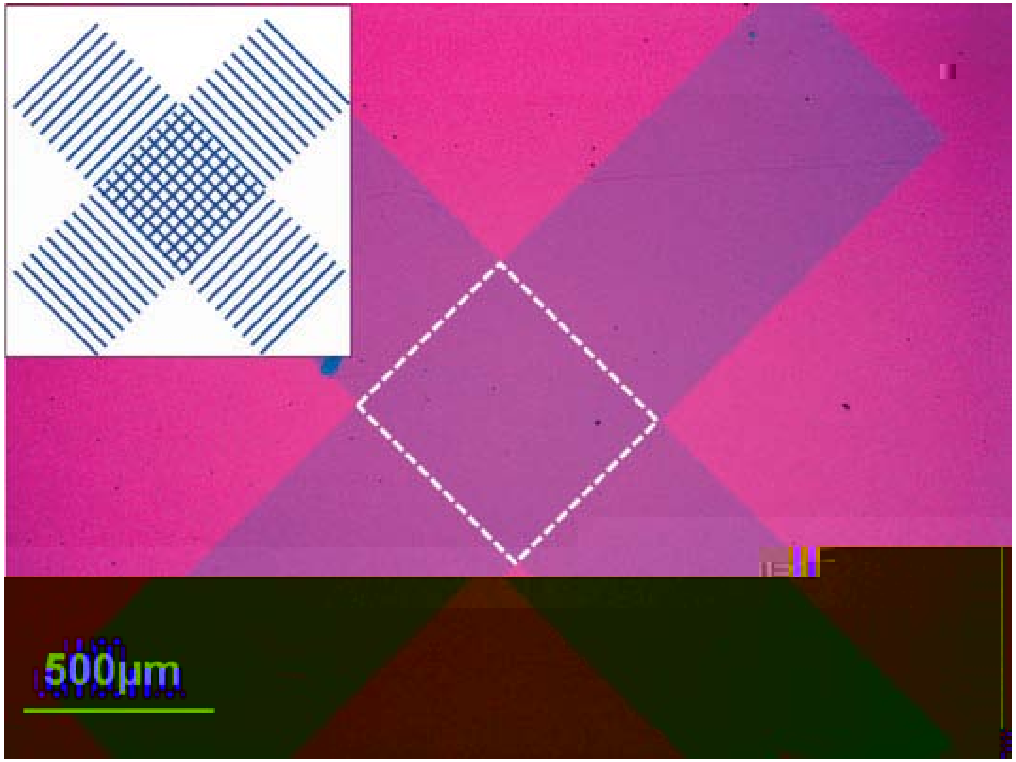
2µm

C.T. Nottbohm et al., J. Vac. Sci. Technol. B 27, 3059 (2009)

Perforated Nanomembranes

Nanosieve fabrication by EUV-IL





M. Schnietz et al., Small 23, 2651 (2009)

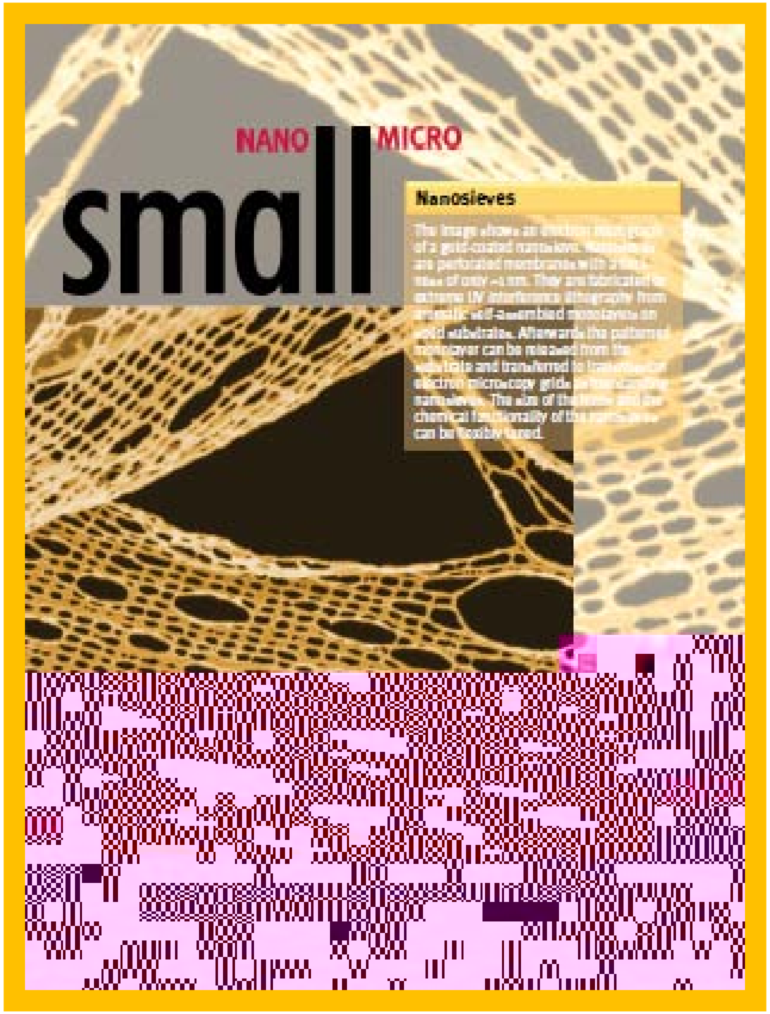
Nanosieve membranes with a thickness of 1 nm via EUV-IL

200 x 225 nm period,

hole diameter = 138 ± 17 nm

M. Schnietz et al., Small 23, 2651 (2009)

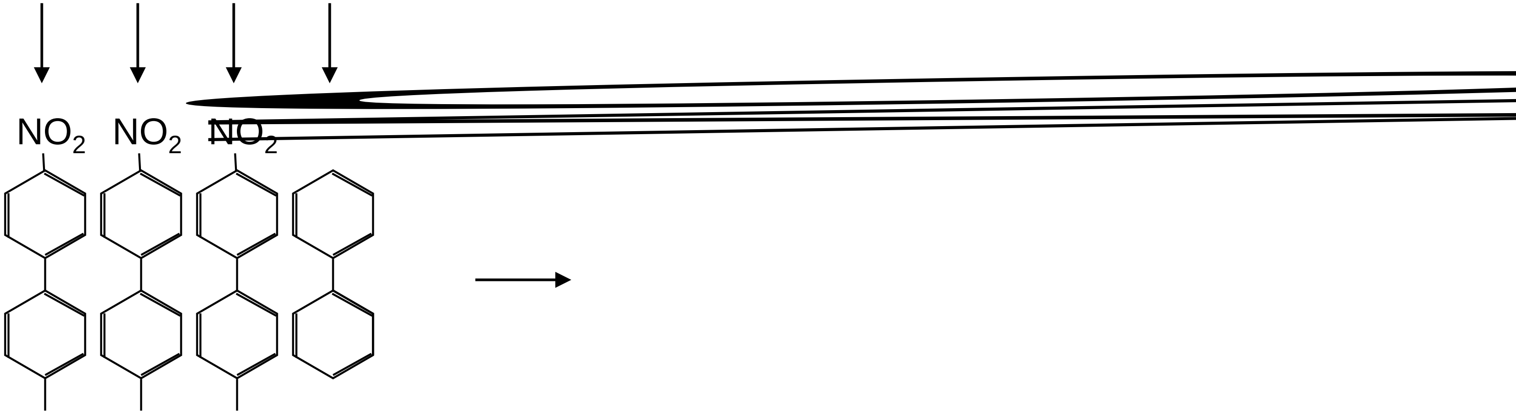
Freestanding nanosieve coated with 5 nm Au



M. Schnietz et al.,
Small 23, 2651 (2009)

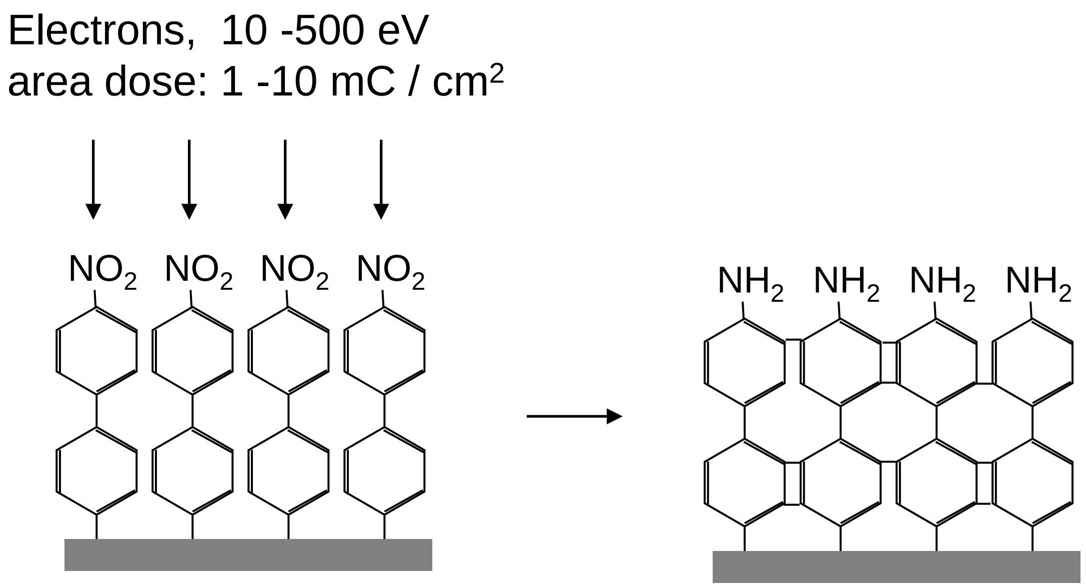
Electron induced cross-linking and NO_2 to NH_2 conversion
"Chemical Lithography"

Electrons, 10 -500 eV
area dose: 1 -10 mC / cm^2



Appl. Phys. Lett. 75, 2401 (1999)

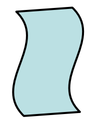
Electron induced cross-linking and NO_2 to NH_2 conversion "Chemical Lithography"



Appl. Phys. Lett. 75, 2401 (1999)

Adv. Mater. 12, 805 (2000)

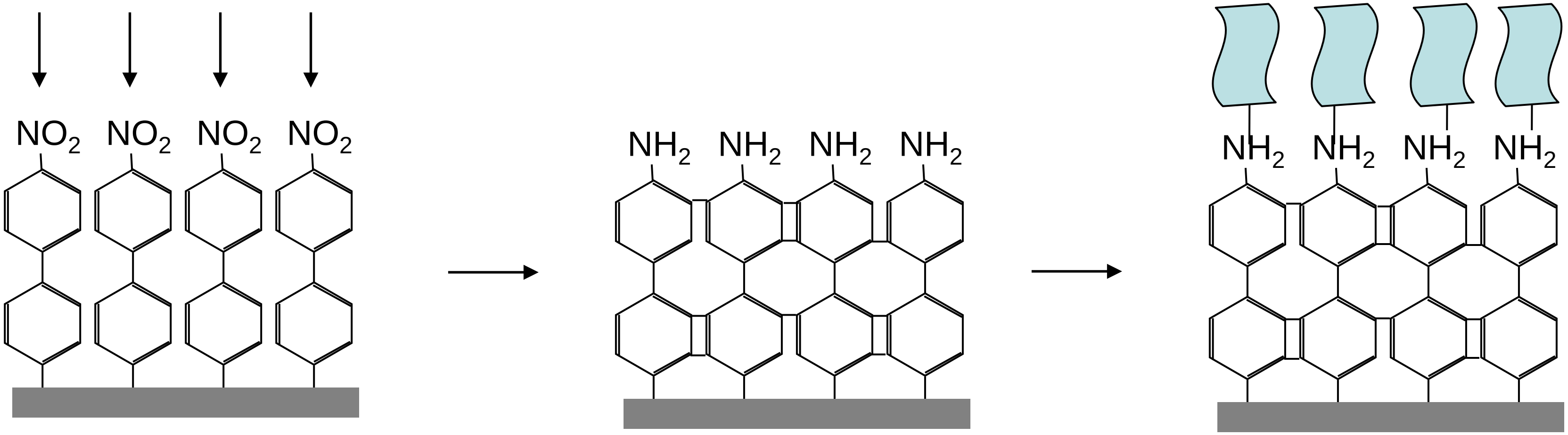
Electron induced cross-linking and NO_2 to NH_2 conversion: Chemical lithography and subsequent functionalisation



= **Molecules binding to NH_2 group**

- **polymers**
- **proteins**
- **dyes**
- **...**

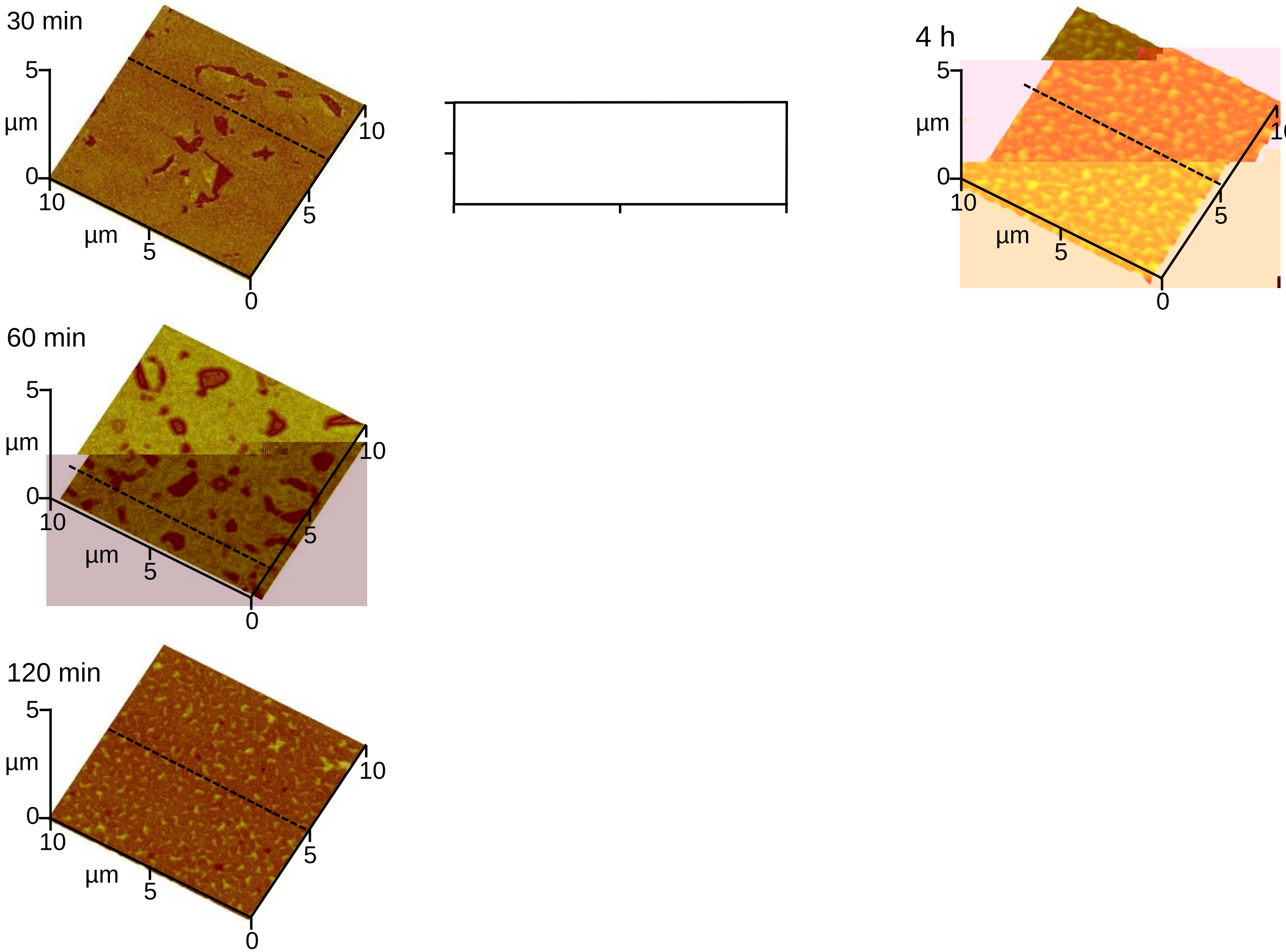
Electrons, 10 -500 eV
area dose: 1 -10 mC / cm^2



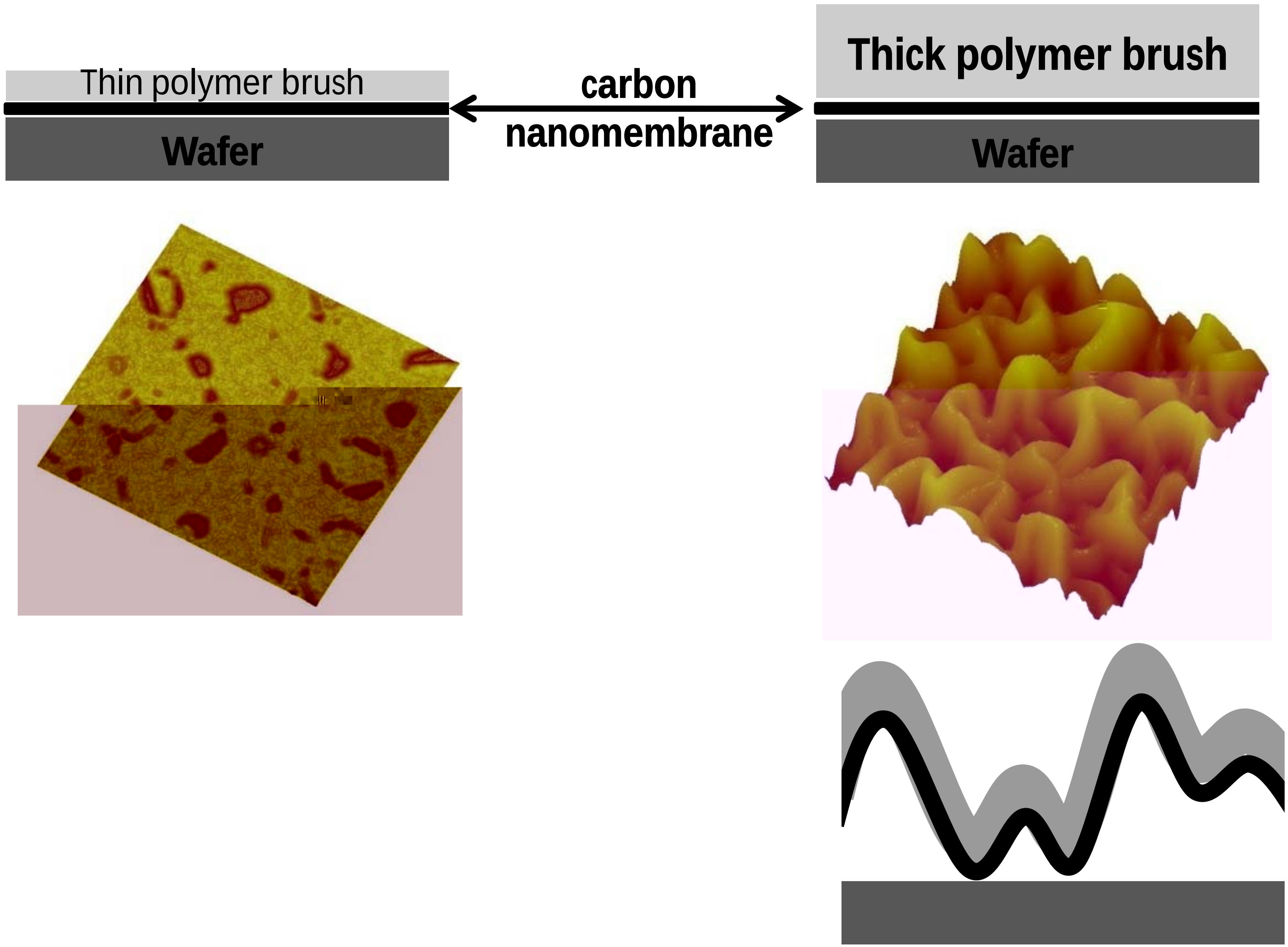
Adv. Mater. **12**, 805 (2000)
Small **3**, 2114 (2007)

Polymer Carpets

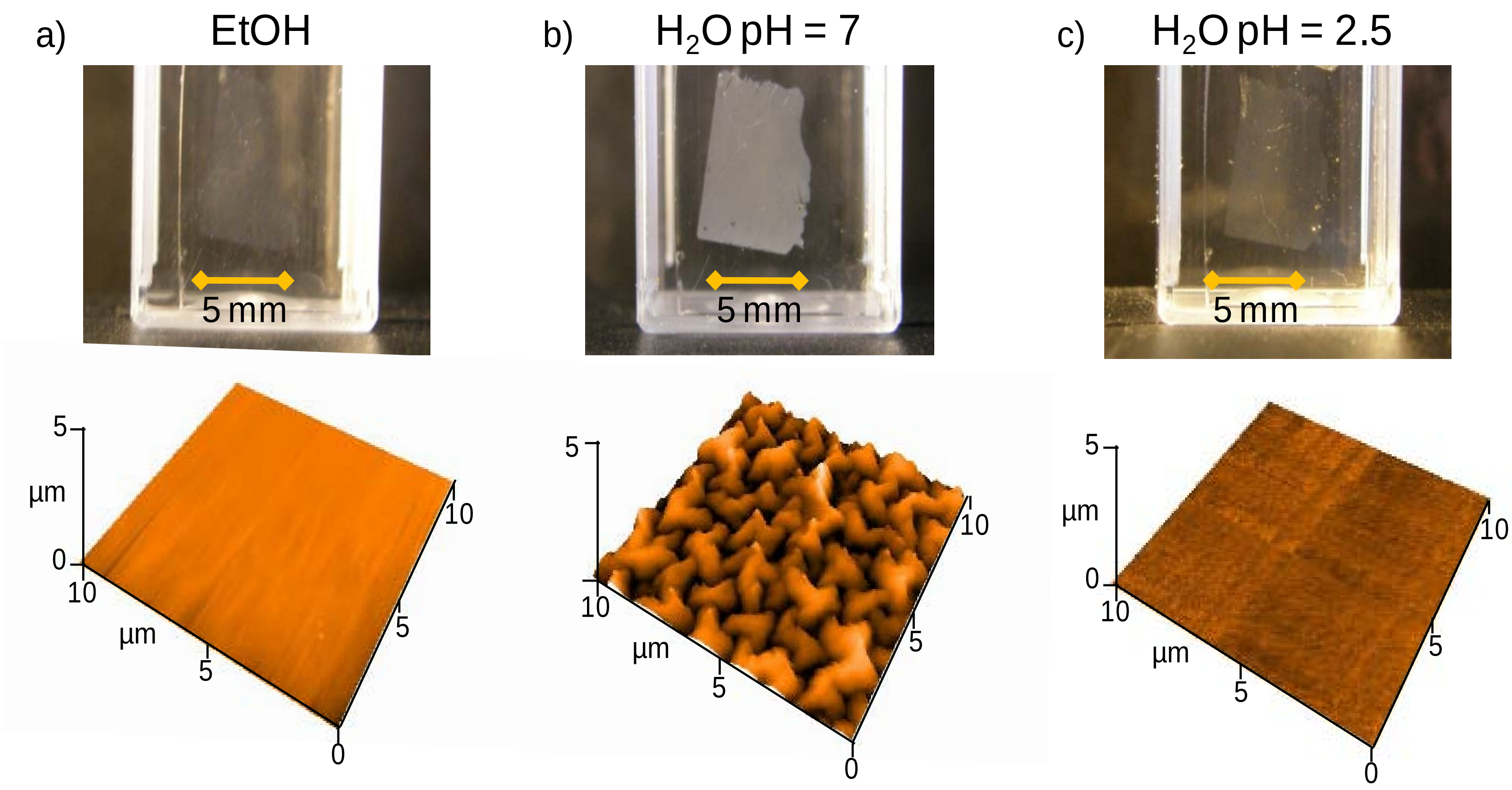
Small 6, 1623 (2010)


30 min
60 min
120 min
4 h
5
µm
0
10
5
0

Buckling of Polymer Carpets



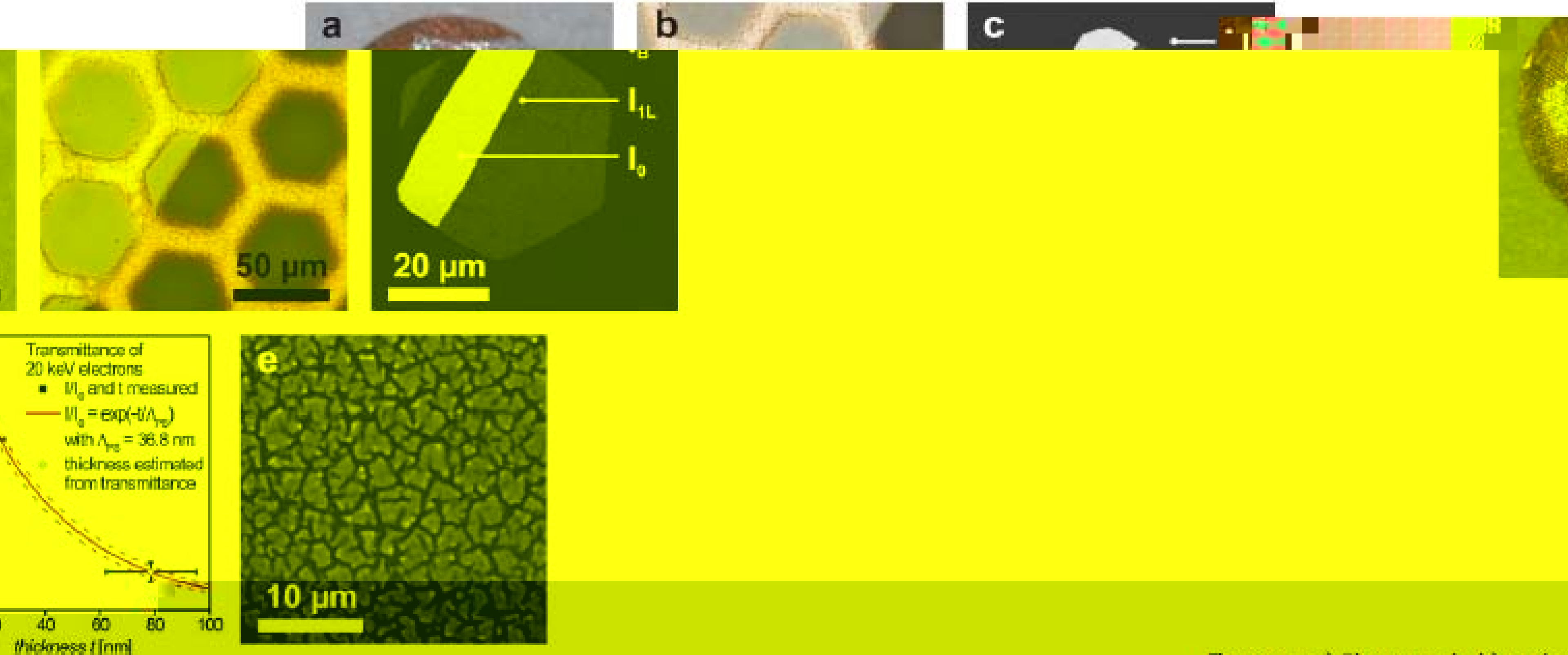
Building a Sensor (and Actuator) by Buckling of Polymer Carpet



Photographs and AFM measurements of P4VP carpets in a) ethanol, b) water at pH 7 and c) water at pH 2.5.

Small 6, 1623 (2010)

Electron Transmission through freestanding Polymer Carpets

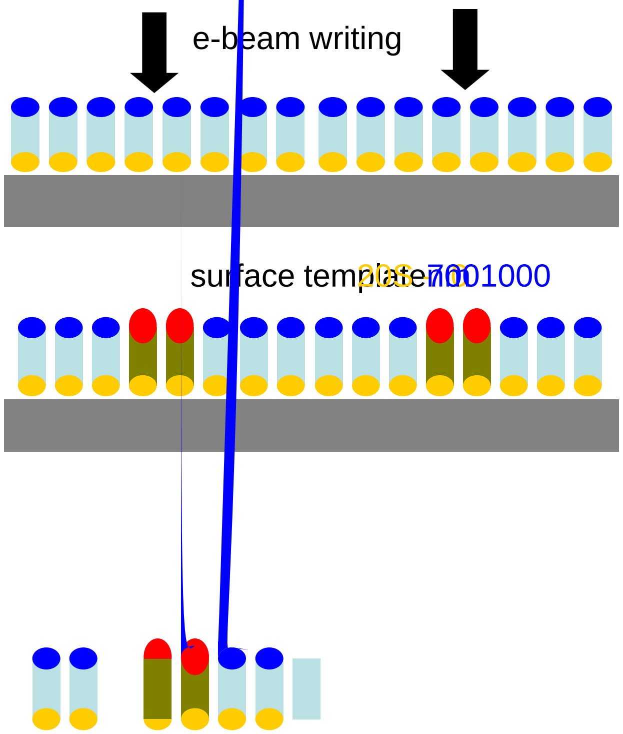


STEM image of freestanding PS carpets. d) The transmittance of 20 keV electrons was
th as in (c). An attenuation length of 36.8 nm (solid red line) ±2.6 nm (dashed lines) was
at higher magnification.

Figure 7. a) Photograph, b) optica
determined from STEM images of
calculated. e) STEM image of a fre

Small 6, 1623 (2010)

Immobilization of biomolecules

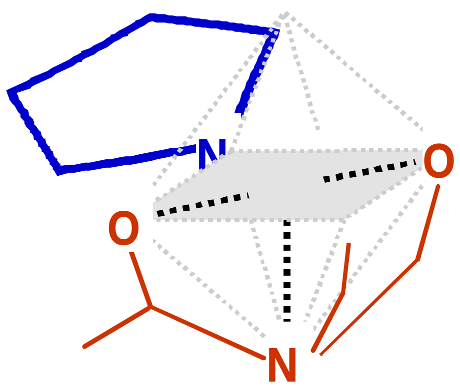


NTA/His-tag interaction: molecular tweezers

histidine

histidine tag (His-tag)

{easily introduced into proteins by genetic engineering



NTA

nitrilotriacetic acid (NTA)

{high specificity for neighboring histidine residues

{easily functionalized

reversible binding

imidazole
ETDA
low pH

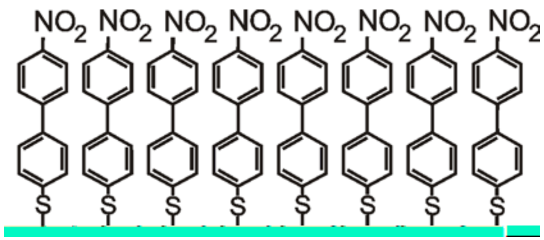
high affinity by utilization of

multivalent chelators: bis-NTA,tris-NTA

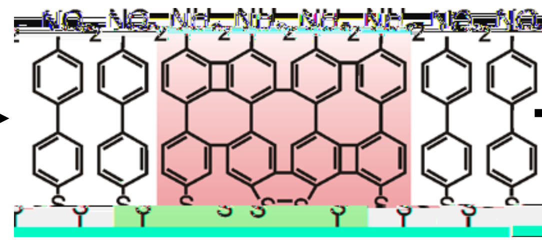
F.H. Arnold, Metal -affinity protein separations, Academic Press, 1992
S. Lata, A. Reichel, R. Brock, R. Tampé, J. Piehler, JACS 127 (2005) 10205

Assembly of the structured chips: schematic representation

SAM formation



e-beam/EUV lithography

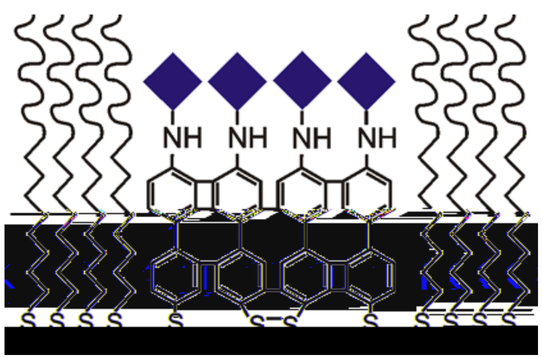


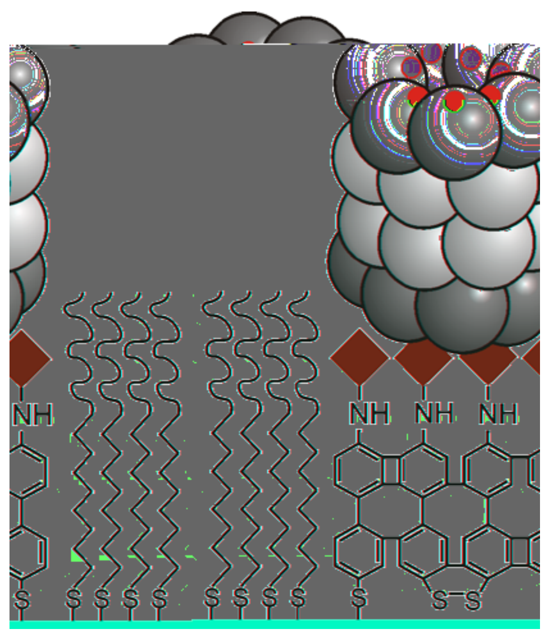
molecular self-assembly
e-beam/EUV lithography
chemical biology
molecular recognition

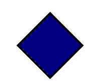
tris -NTA

functional immobilization of His $_6$-taged proteins

grafting of multivalent chelators and generation of the protein repellent matrix

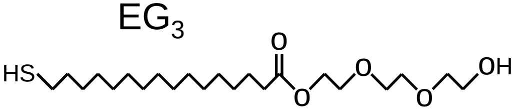




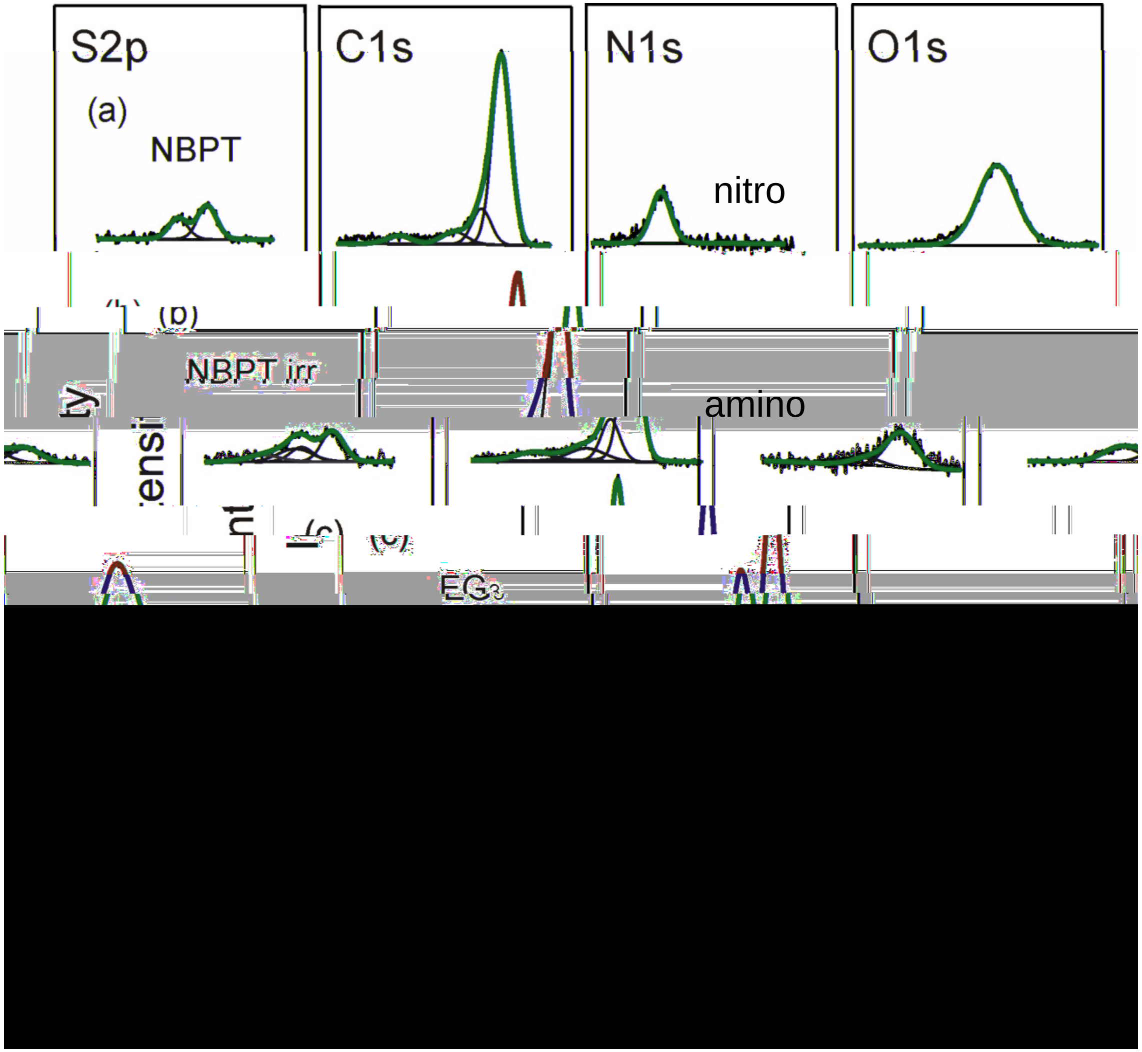
 =

o

EG$_3$



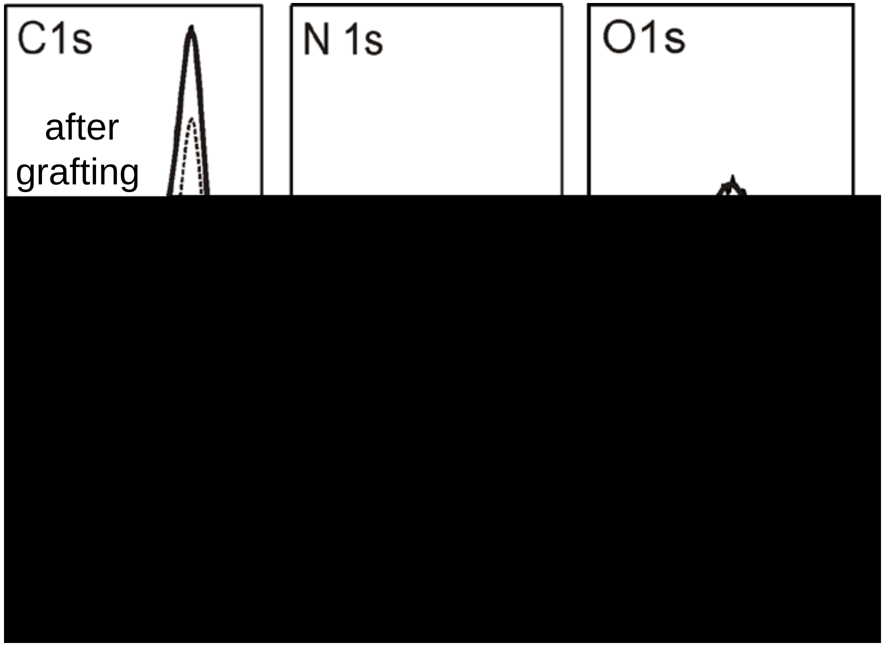
XPS characterization of the elemental components of the chip' surface



different types SAMs

A.Turchanin, A. Tinazli , M. El-Desawy , H. Großmann, M. Schnietz ,
H. H. Solak, R. Tampé, A. Gölzhäuser, Adv. Mater. 20, 471 (2008)

Grafting of multivalent chelators (tris-NTA)



thickness increase ~ 6 Å

tris -NTA:NBPT ~1:9

experimental C:O:N =11.2:3.5:1

theoretical C:O:N =11.1:3.4:1

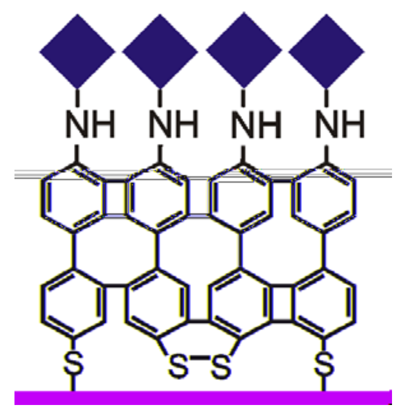
C1s^{I} 284.9 eV (alkane-like groups)

C1s^{II} 286.8 eV (N-C bonds)

C1s^{III} 288.9 eV (carboxylic groups)

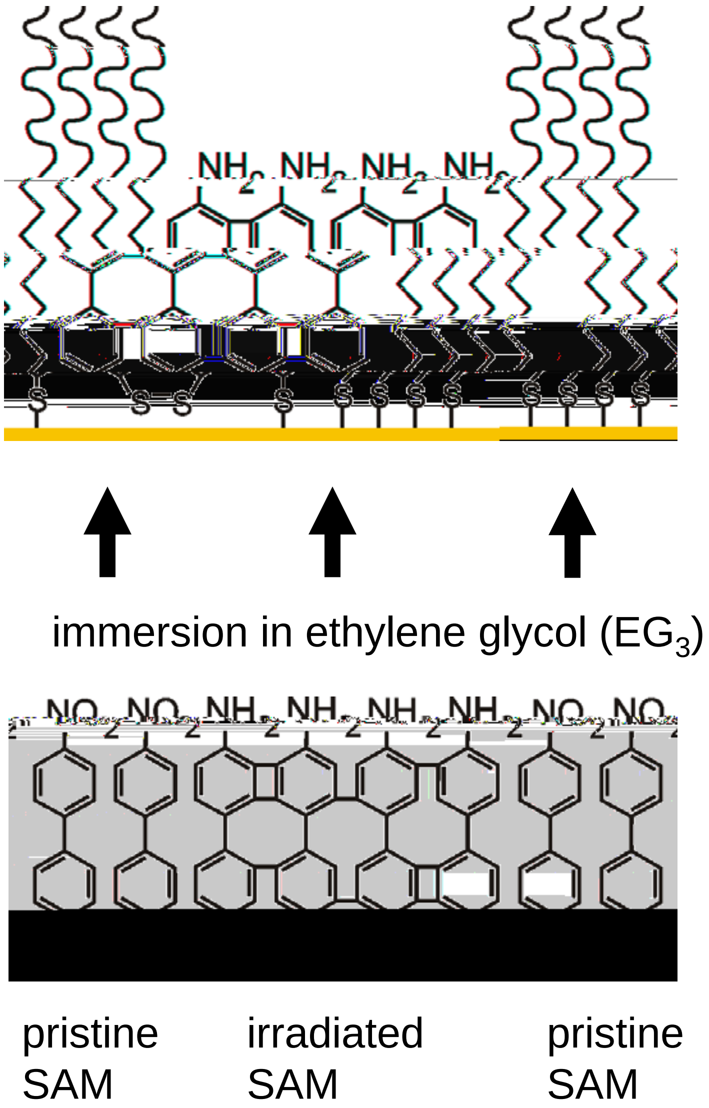
N1s 399.8 eV (amine groups)

O1s 531.9 eV (carboxylic groups)



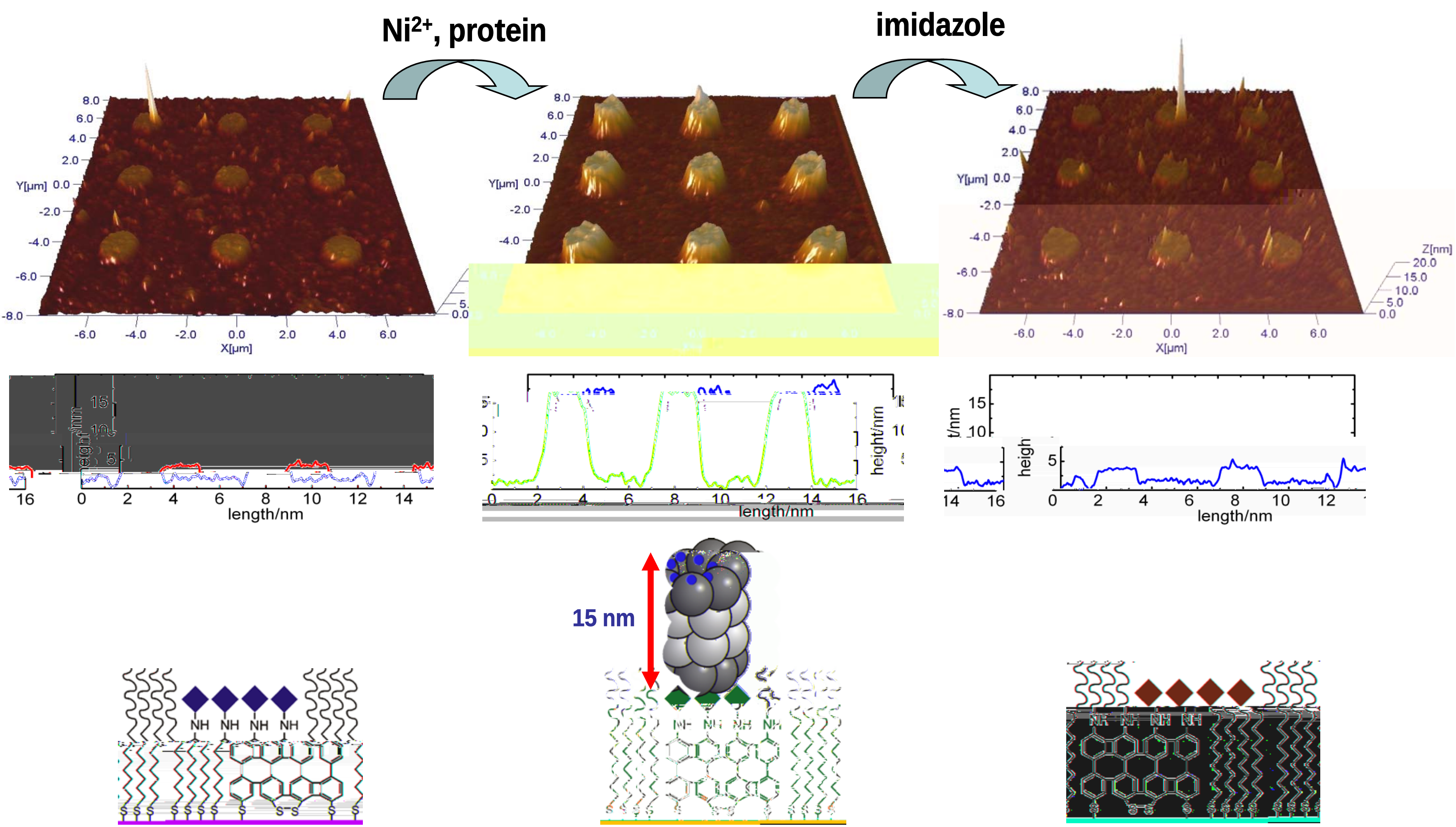
Adv. Mater. 20, 471 (2008)

Generation of protein repellent matrix by exchange



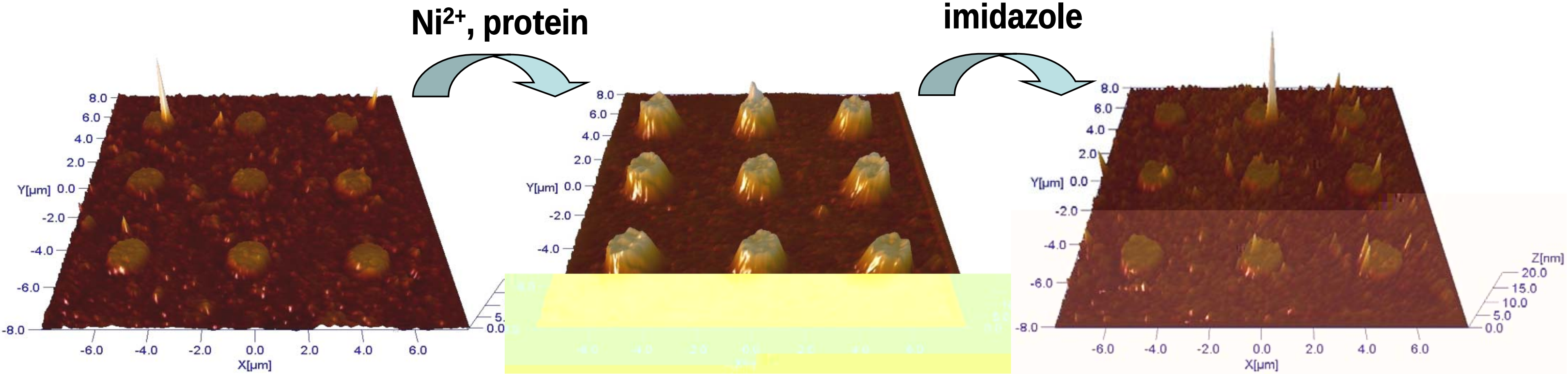
Protein chip functioning: an *in situ* AFM study

Chips' surface in buffer | **Immobilization of proteins** (20S His_6-tagged proteasome) | **Regenerated chip**



Protein chip functioning: an *in situ* AFM study

Chips' surface in buffer | **Immobilization of proteins** (20S His_6-tagged proteasome) | **Regenerated chip**



structured
specific
highly parallel
highly affine
oriented
reversible

A.Turchanin et al.
Adv. Mater. 20, 471 (2008)

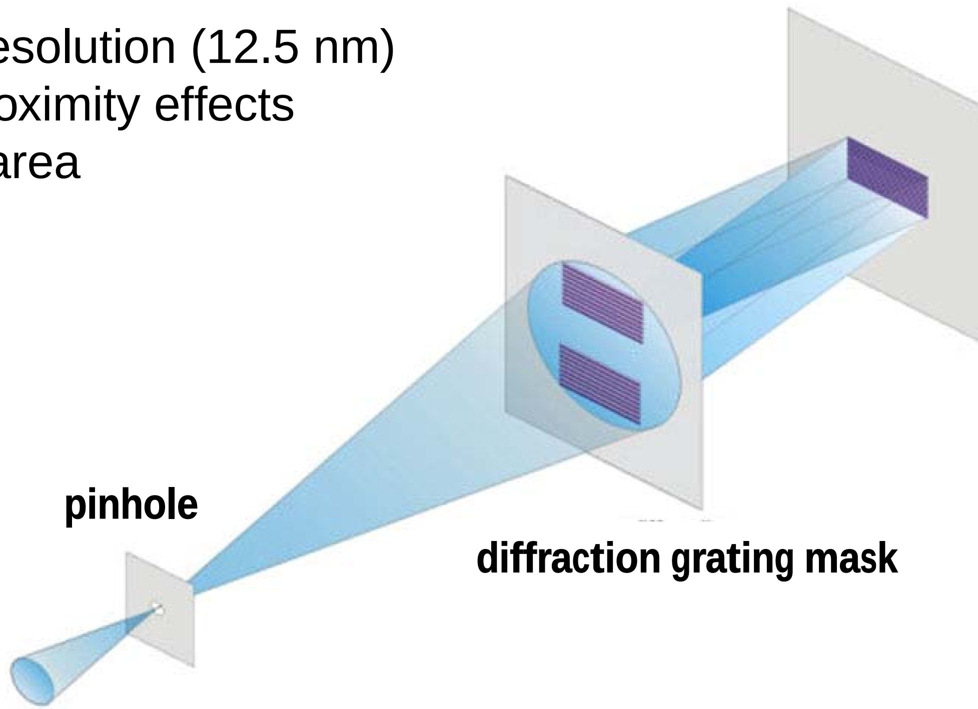
immobilization of protein micro arrays

Down to the single molecular resolution?

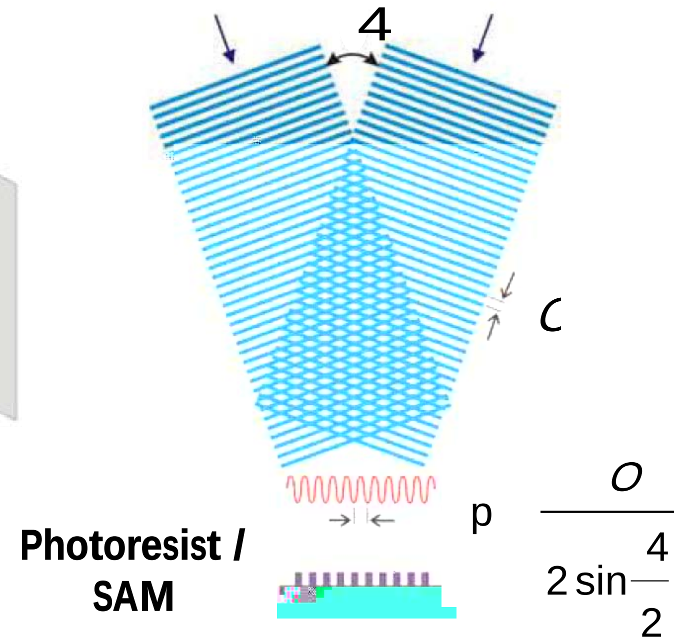
Protein nanopatterns by EUV Interference Lithography

Extreme UV Interference lithography (EUV-IL):

- high resolution (12.5 nm)
- low proximity effects
- large area



focused synchrotron irradiation (92.5 eV, 13.5 nm)



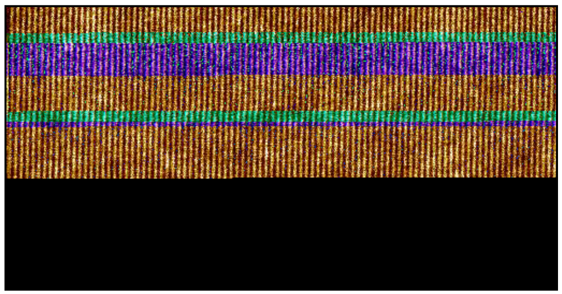
Two coherent beams are forming a linear fringe pattern with a sinusoidal intensity distribution.

H. H. Solak, Microelectronic Engineering 78-79 (2005) 410-416

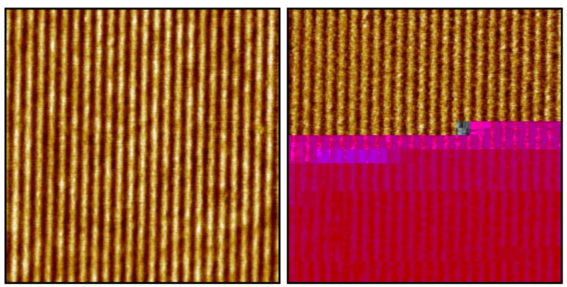
High resolution chemical patterns by EUV-IL: AFM

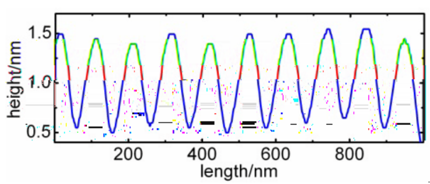
50 nm lines

(a) nitro/amino lines, **topography, 10 × 5 μm^2**

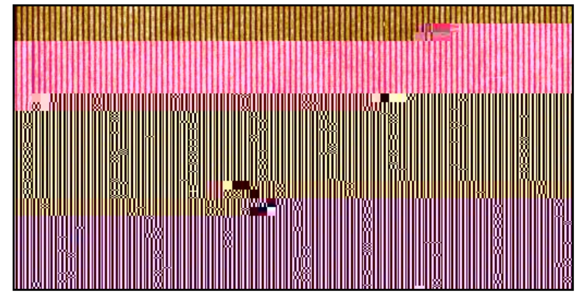


topography (left) and phase contrast (right), 2.5 × 2.5 μm^2

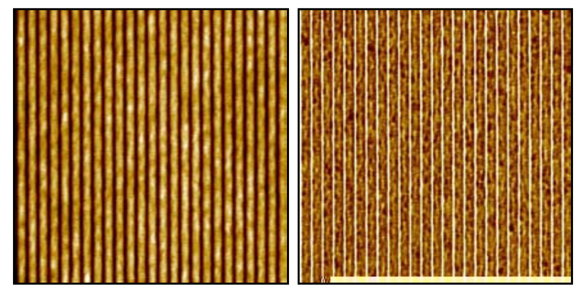


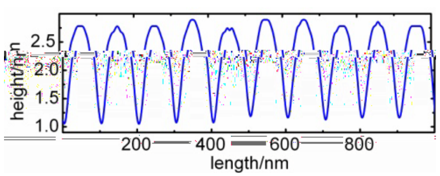


(b) EG_3-OH /amino lines, **topography, 10 × 5 μm^2**



topography (left) and phase contrast (right), 2.5 × 2.5 μm^2



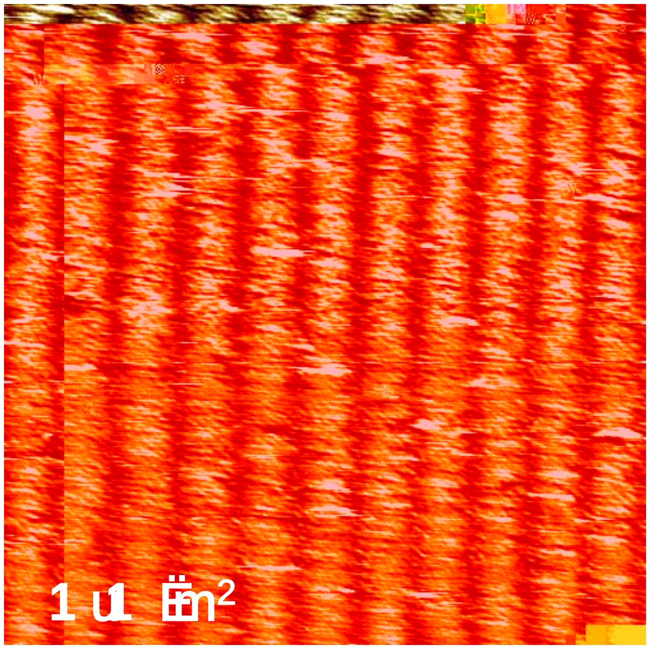


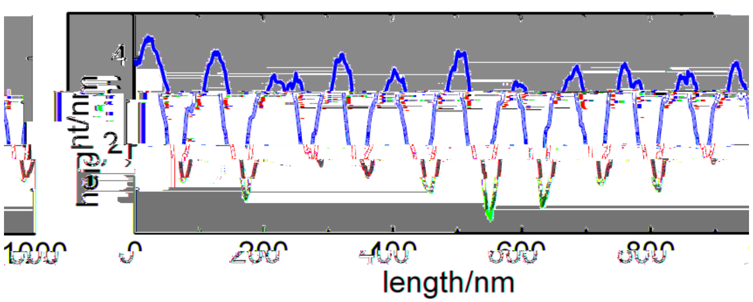
A. Turchanin, M. Schnietz, M. El- Desawy, H. H. Solak, C. David, A. Gölzhäuser, Small 3, 2114 (2007)

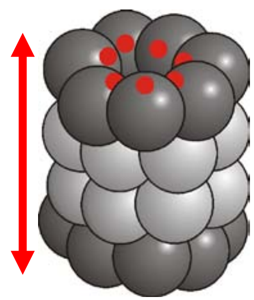
Immobilization of protein nanoarrays : in situ AFM characterization

Proteasome lines

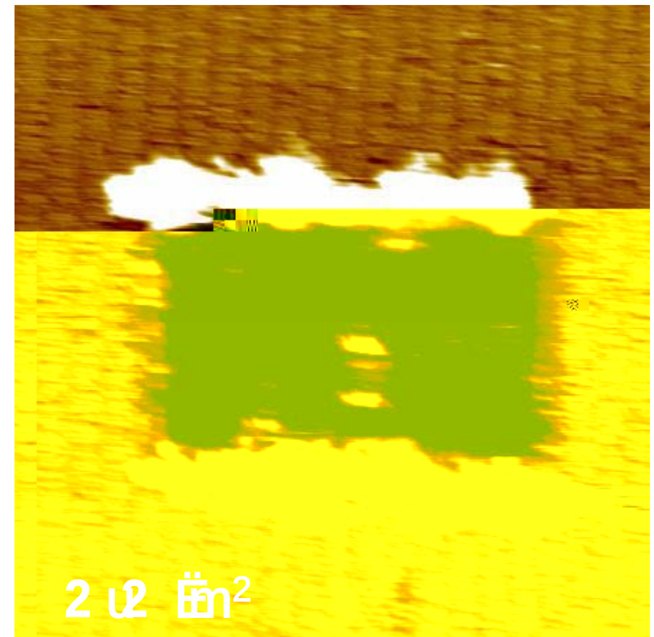
100 nm period

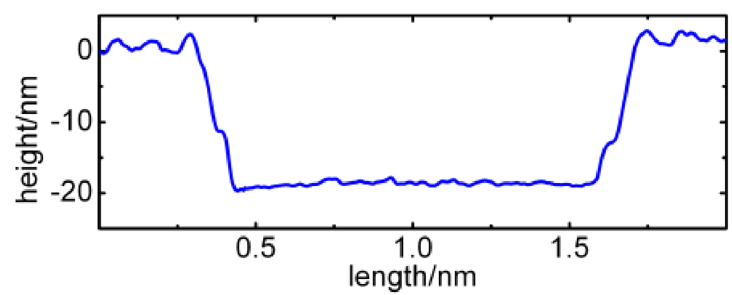






Protein lithography

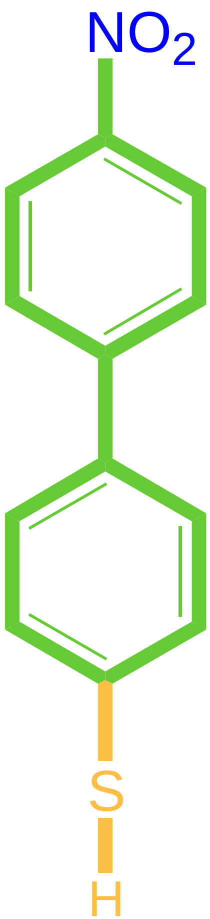


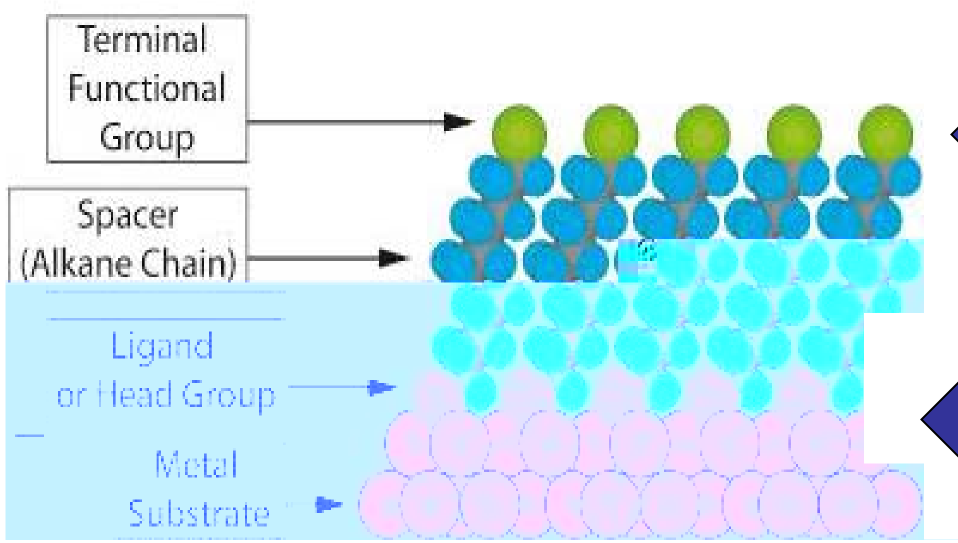


A.Turchanin et al., Adv. Mater. 20, 471 (2008)

Bifunctional Nanomembranes: „Janus Membranes“

SAMs have 2 functional groups!



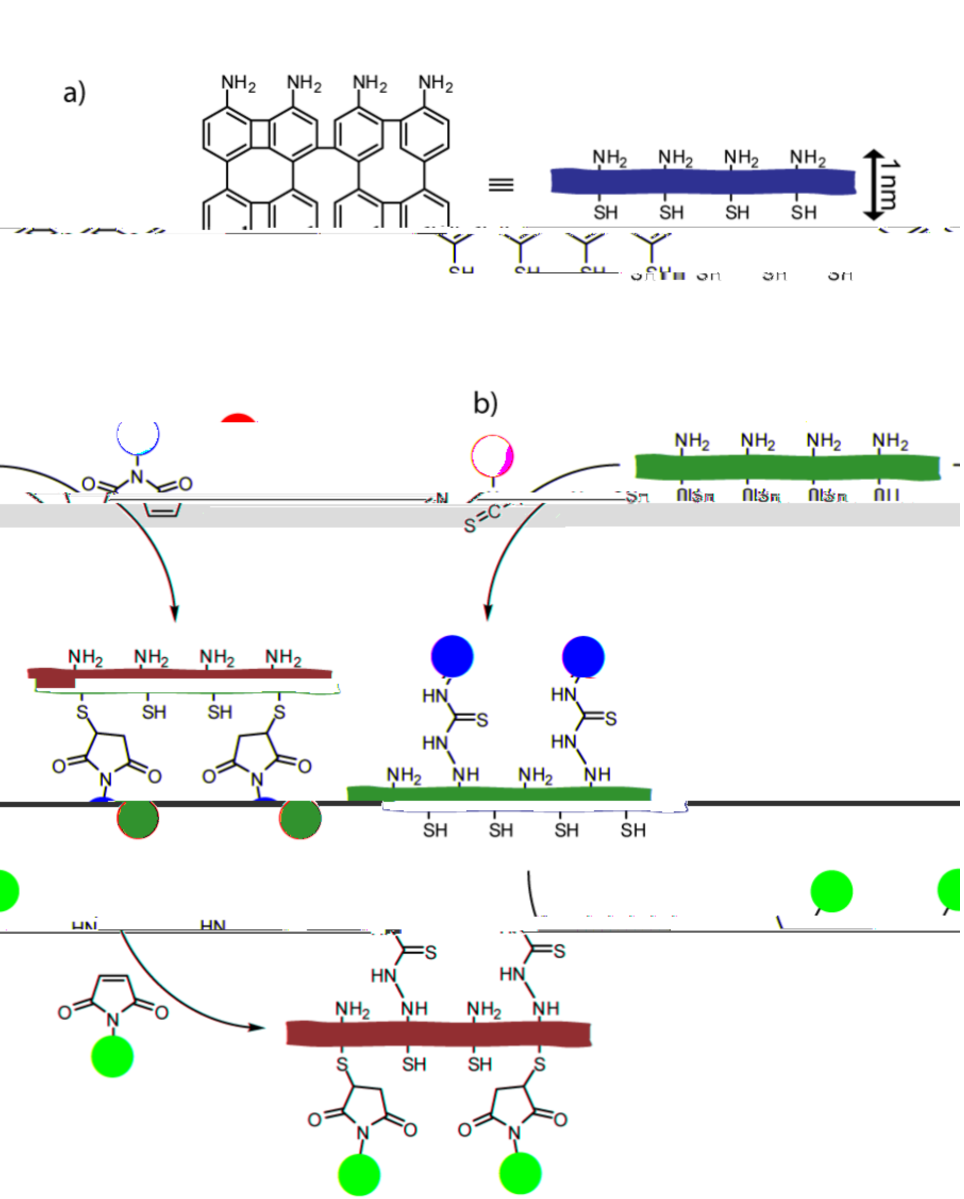


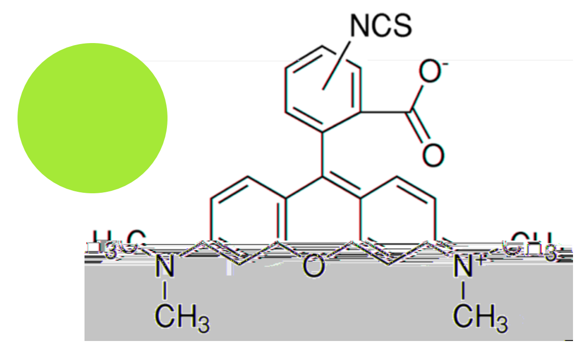
accesible for chemistry

buried

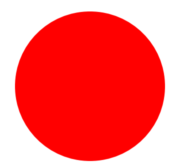
Converting the directionality of the SAM into the directionality of a 2D nanomembrane....

Different fluorescent molecules on top and bottom of membrane





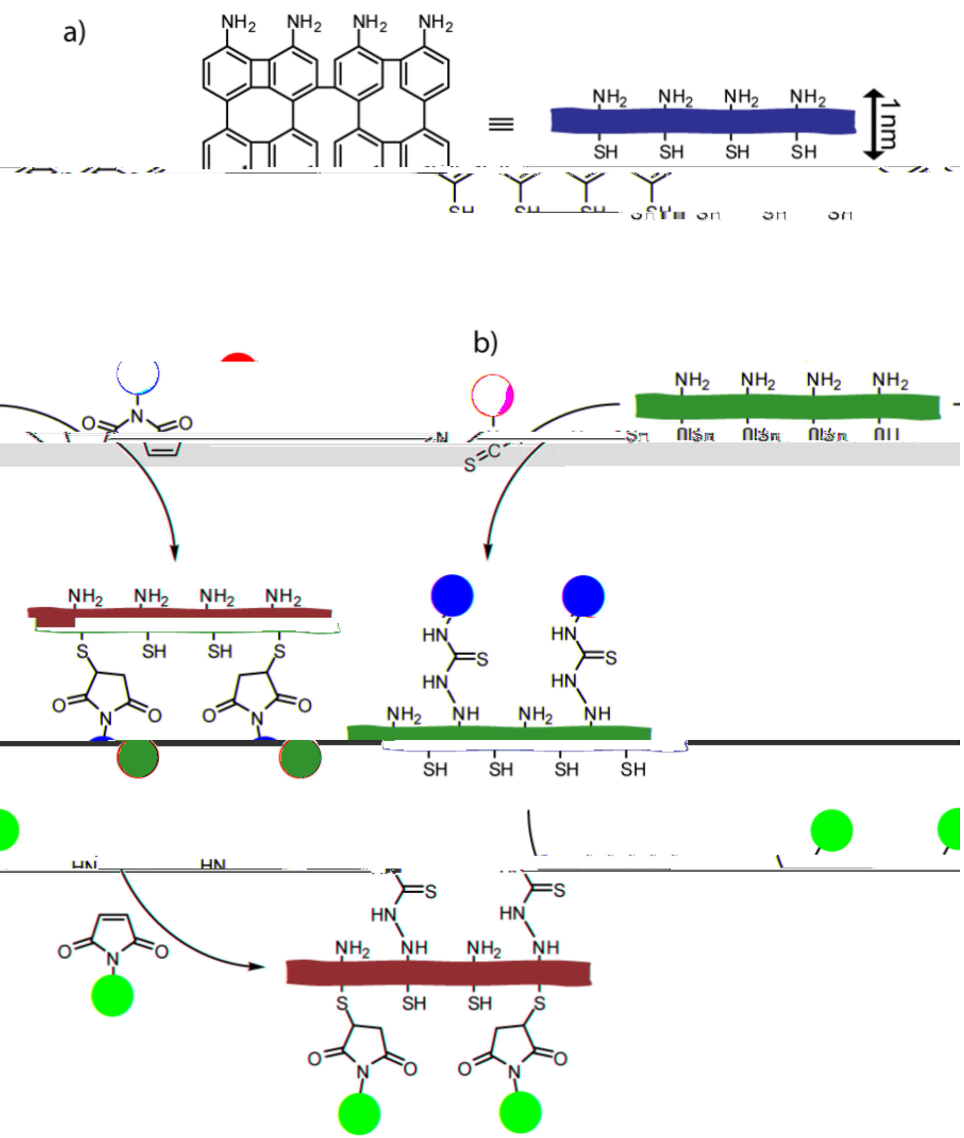
tetramethylrhodamine isothiocyanate (TMR)

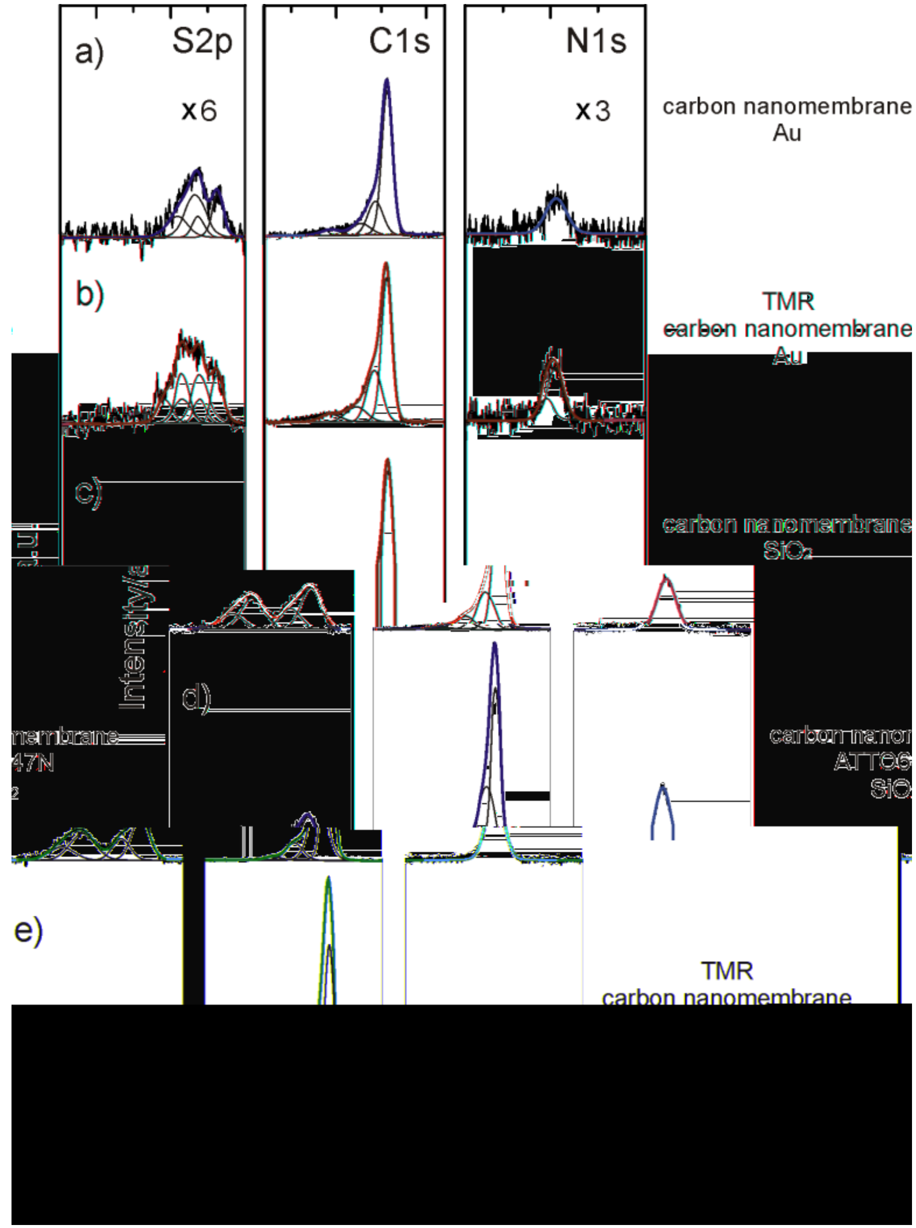


ATTO647N

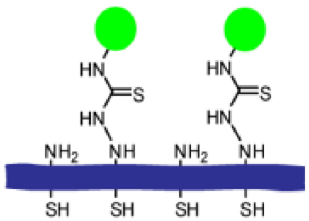
Zinkun Zheng

Monitoring molecular coupling by XPS



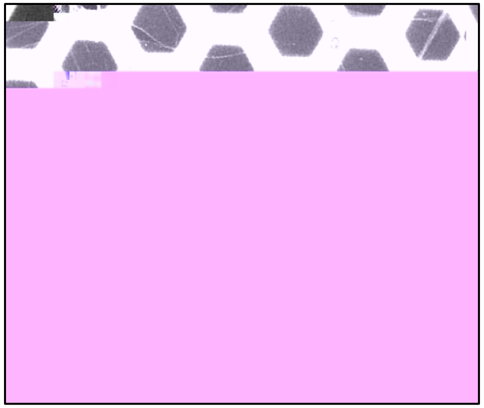


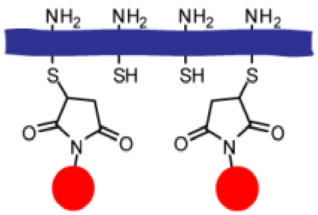
Flourescence detection of TMR and ATTO



a)

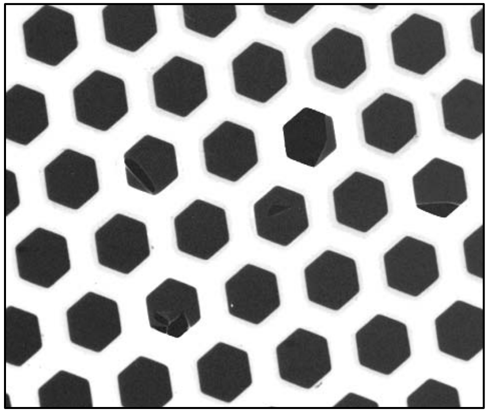
b)





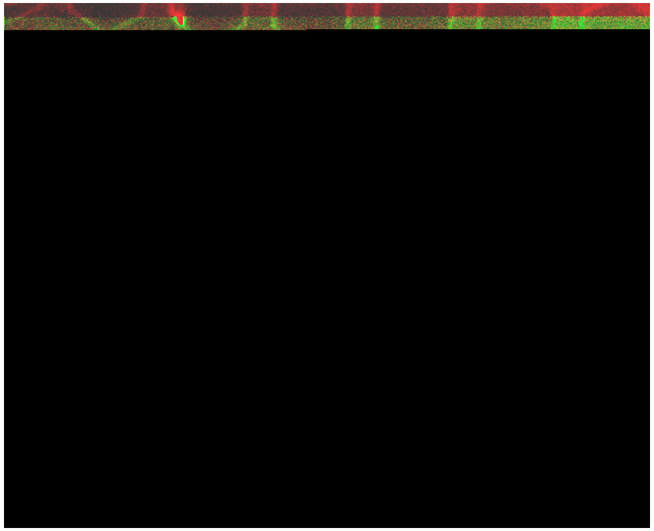
c)

d)

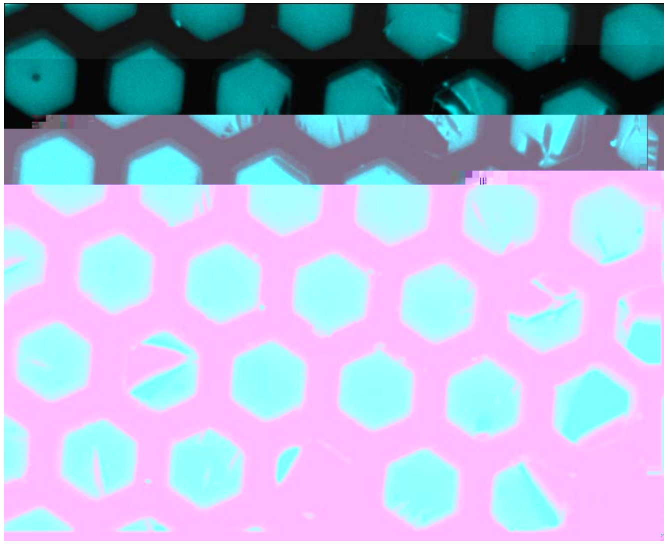


Step 3: Coupling of TMR to Top and ATTO647N to Bottom

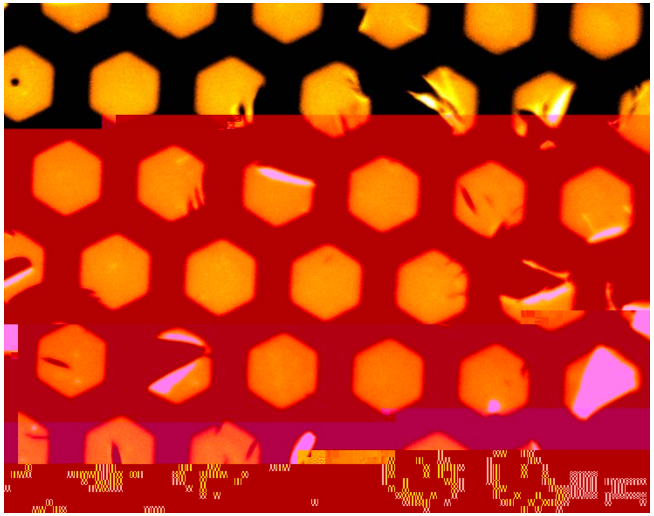
Fluorescence TMR



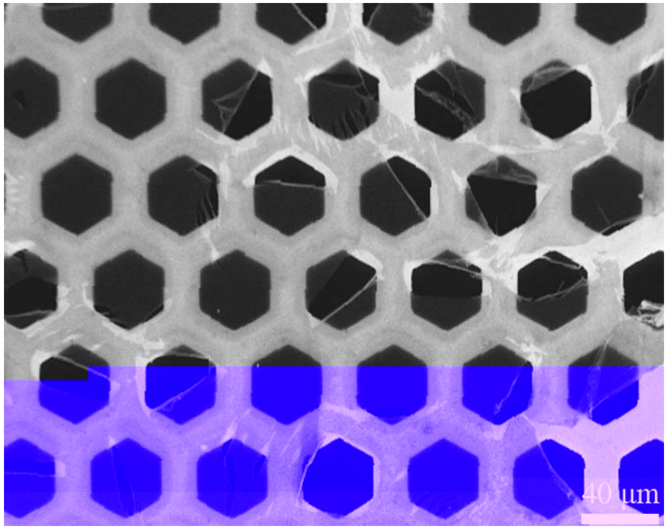
Fluorescence ATTO647N



FRET (Förster Transfer)



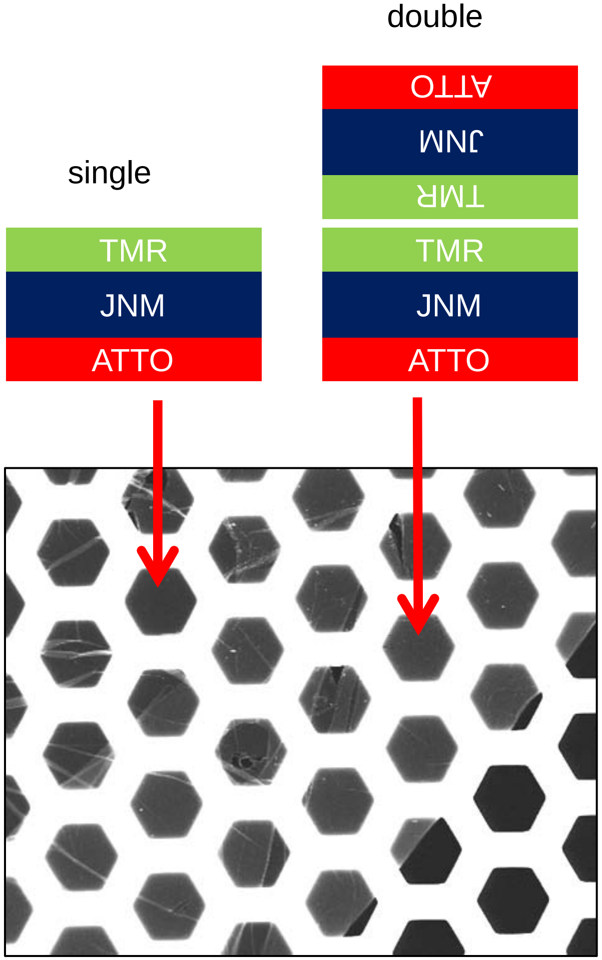
SEM



Angewandte Chemie, In press

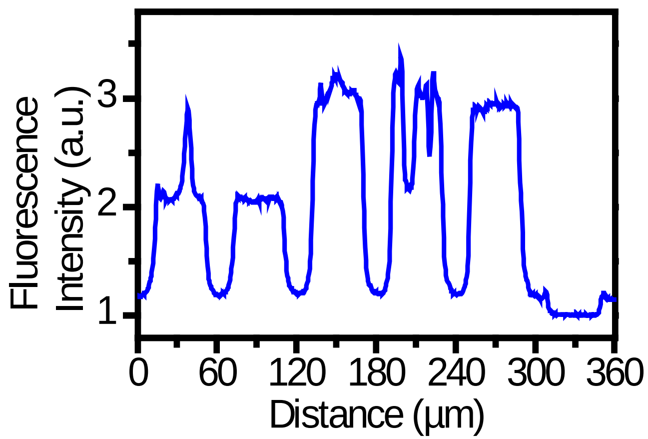
Single and double layers

a)



b)

c)



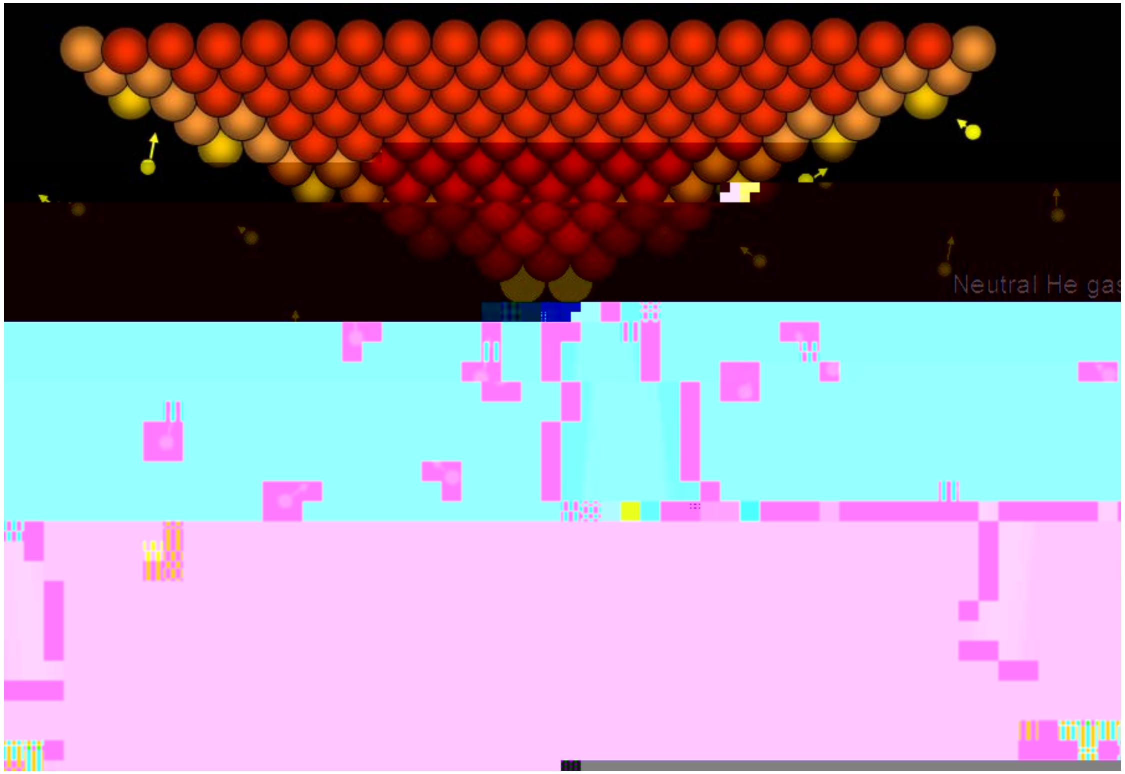
Angewandte Chemie, In press

Is there a better imaging technique ?

Helium Ion Microscope

- World’s first commercially available Helium Ion Microscope (Carl Zeiss)
- Analogous to a SEM but uses Helium ions instead of electrons
- Image formed using secondary electrons and backscattered ions

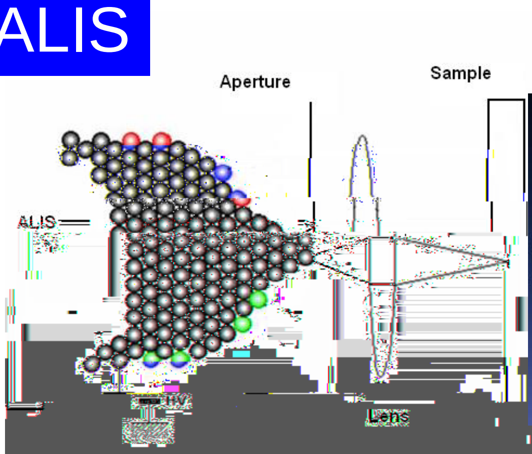
ALIS – Atomic Level Ion Source

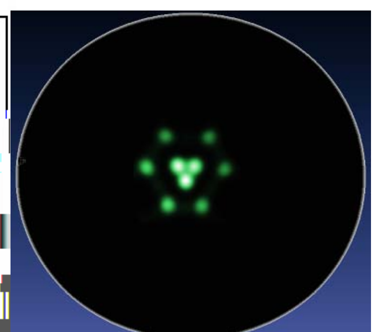


ALIS – Atomic Level Ion Source

FIM

ALIS





Field Ion microscope:

ƒ Small emitters

ƒ Beam current shared among hundreds or thousands of atom

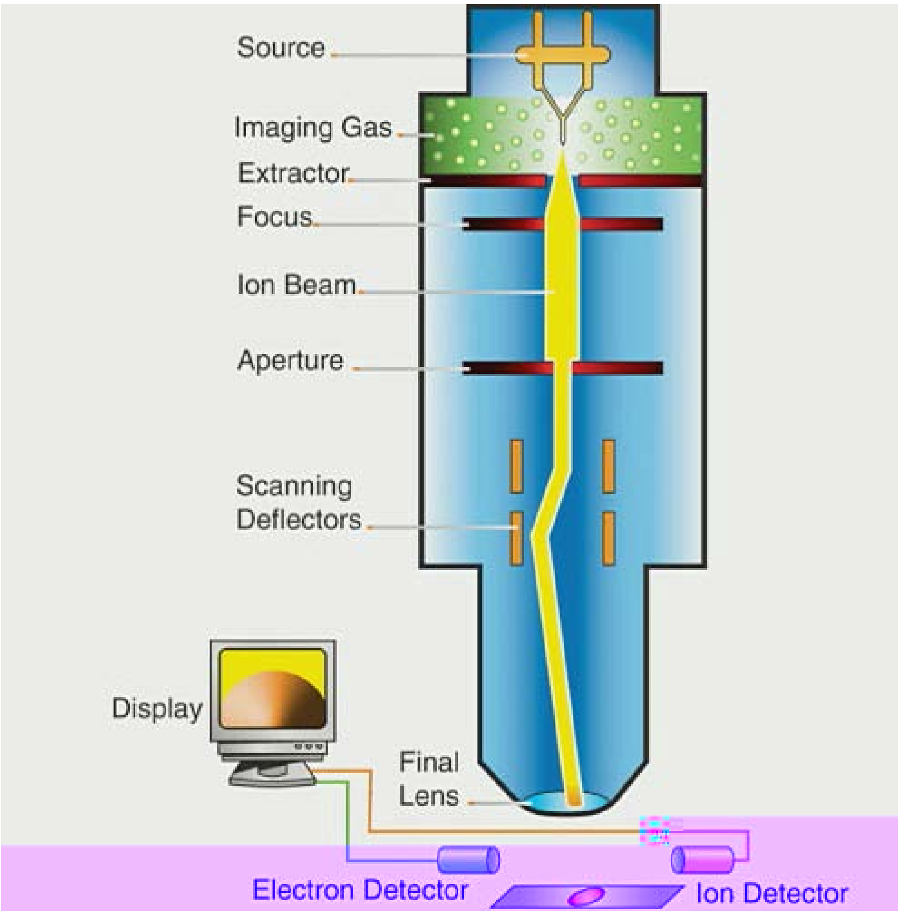
ALIS:

ƒ 3 atom shelf called the “trimer” created through field evaporation

ƒ Single atom selected for final probe

ƒ Source size < 1 Atom diameter

Column Architecture & Uniqueness



Architecture:

- Electrostatic optics similar to SEM / Ga FiB

[redacted]nique:

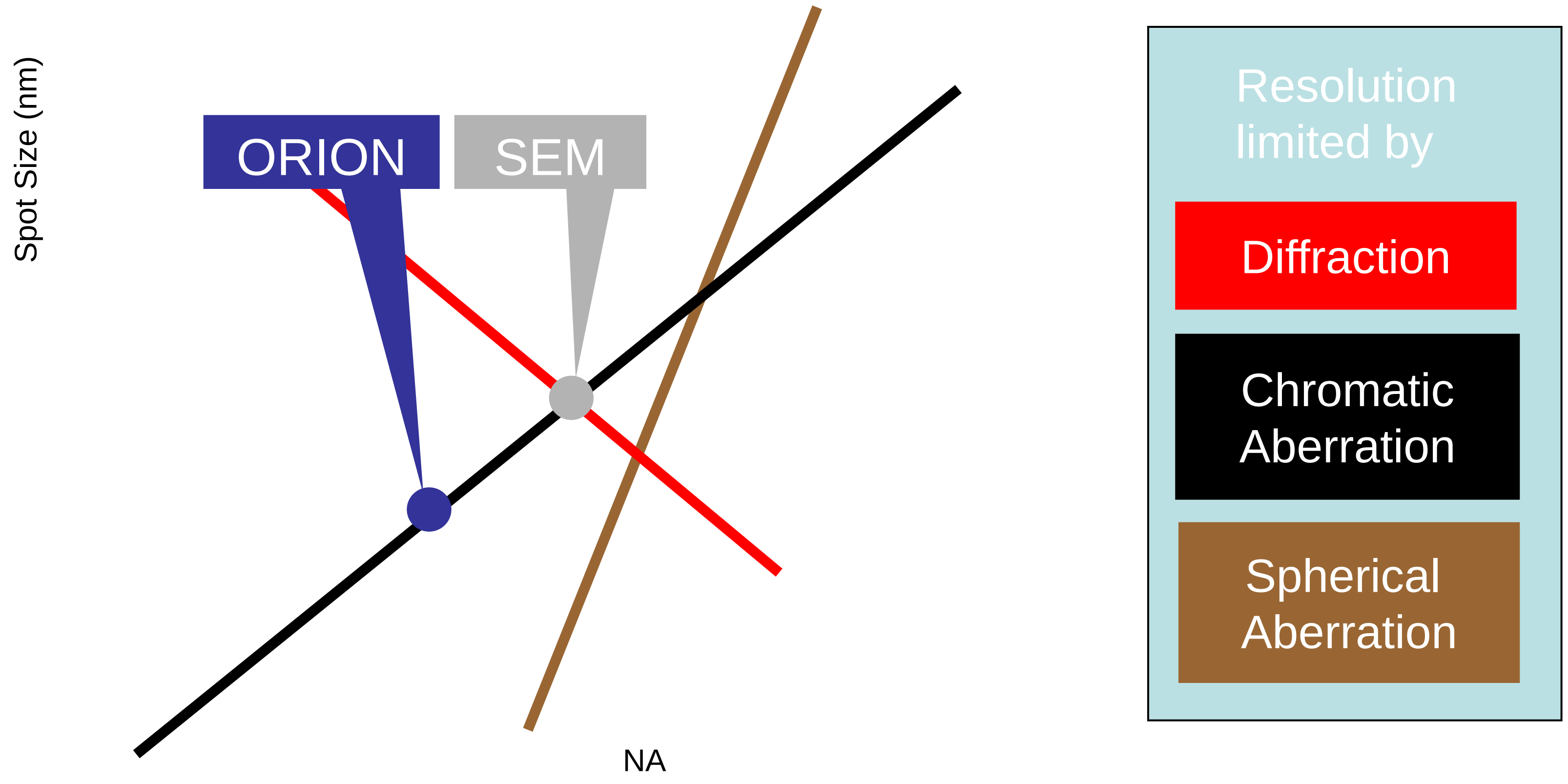
- He Ions:
  - Wave Length (Resolution)
  - Sample Interaction
  - Contrasts
  - Surface Sensitivity
  - Charging

- So[redacted]rce:

Brightness (Resolution/DoF)

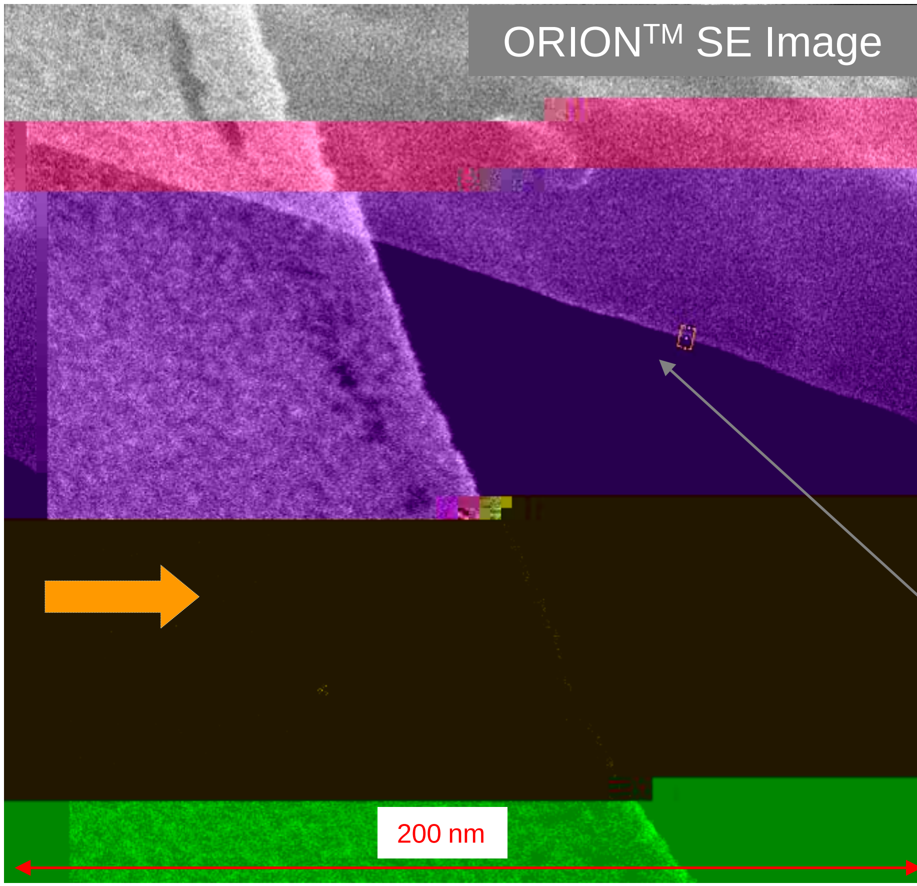
ORION™ HIM Ultra High Resolution

Down to 0.2 nm Probe Size



5-10x smaller NA (better Depth Of Field)

ORION™ Resolution Recent Status Update
0.24 nm resolution demonstrated in R&D lab

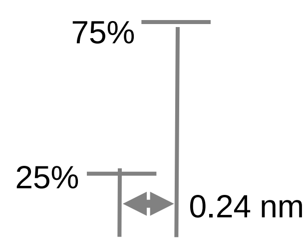


Specimen „Asbestos fibre“ on holy carbon

SE Imaging World Record
Resolution 0.24 nm (+/ - 0.04 nm)

- Working Distance: 6 mm
- TEM like „salt and pepper pattern“ visible on carbon foil
- 0.24 nm resolution measured repeatedly on ORION R&D System

Linescan from edge of Asbestos fibre averaged over 20 neighbouring lines



*upgrade path will be available for Orion Plus customer

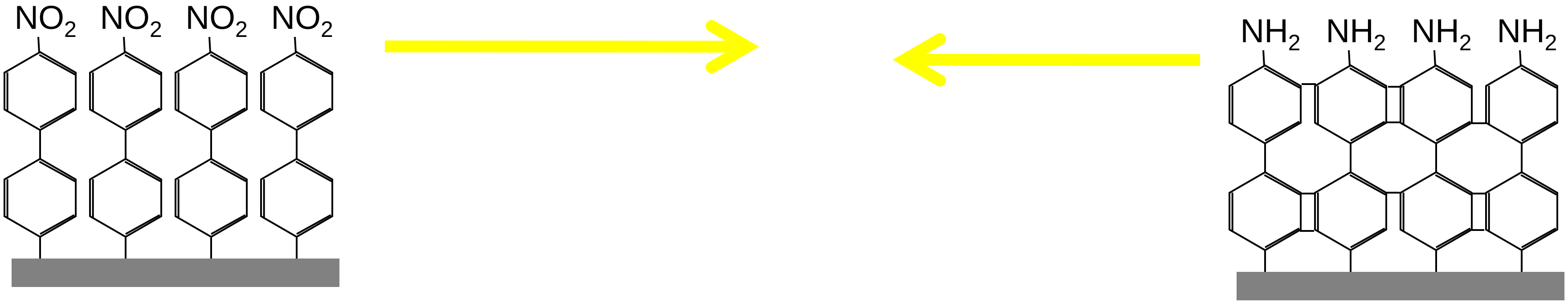
Unique Material Contrast

2µm

2µm

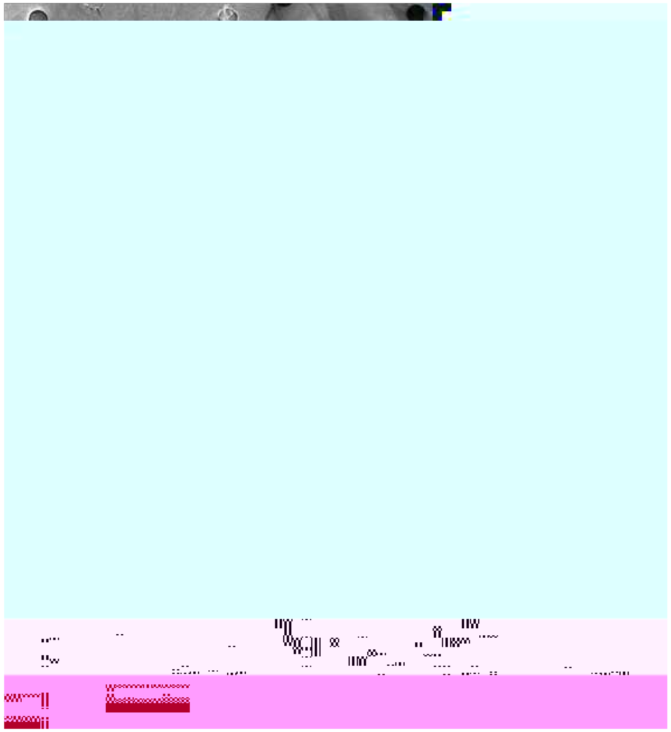
Secondary Electron image from the ORION™ shows superior material contrast in addition to surface detail

Imaging of SAM/Au Surface after Chemical Lithograpy



Visualizing 2-dimensional Nanomembranes

HIM



SEM

Freestanding nanomembranes on holey carbon foil

Quantifoil Holey Carbon Film, He^+ Ion Image

(A. Beyer)

Visualizing 2-dimensional Nanomembranes

SEM

HIM

Universität Bielefeld

Acknowledgements:

Bielefeld group: *Andrey Turchanin, André Beyer, Christoph Nottbohm, Xianghui Zhang, Ishan Amin, Berthold Völkel, Mohamed El-Desawy, Min Ai, Eline Oberländer, Nils Mellech, Heiko Muzik, Mark Schnietz, Matthias Büenfeld, Laxman Kankate, Zinkun Zheng* **http://www.physik.uni-bielefeld.de/pss**
E-Mail: ag@uni-bielefeld.de

Collaborations: *Paul-Scherrer-Institut: Harun H. Solak*
Univ. Bielefeld: Günter Reiss, Andreas Hütten, Mark Heilemann, Markus Sauer
PTB: Reiner Stosch, Peter Hinze, Dirk Weber, Thomas Weimann
Univ. Heidelberg: Wolfgang Eck, Michael Grunze
Univ. Frankfurt: Helge Großmann, Robert Tampé
KIT Karlsruhe: Christof Wöll
Univ. Marburg: Gregor Witte, Daniel Rhinow, Norbert Hampp
RWTH Aachen: Alla Solugubenko, Joachim Mayer
TU Dresden: Rainer Jordan, Marin Steenackers
NCEM Berkeley: Christian Kisielowski
Carl Zeiss: Larry Scipioni, Frank Stietz

EUROPEAN SCIENCE FOUNDATION